Grant Number: RG/2011/BS/03

Title of the Project

Synthesis and characterization of novel polymer electrolytes with possible applications in electrochemical devices such as rechargeable batteries, supercapacitors and solar cells.

Principal Investigator: Dr. (Mrs) V.A. Seneviratne

Co-Investigators: Dr. L.R.A.K. Bandara

Section 1

Information regarding Project/Project Personnel:

i. Grant Number : RG/2011/BS/03

ii. Title of the Project: Synthesis and characterization of novel polymer electrolytes with possible applications in electrochemical devices such as rechargeable batteries, supercapacitors and solar cells.

iii. Principal Investigator: Dr. (Mrs) V.A. Seneviratne

iv. Co-Investigators: Dr. L.R.A.K. Bandara

v. Institute where Research is being carried out: Department of Physics, University of Peradeniya.

vi. Date of award: 15/09/2011

vii. Date of Completion of Project: 13/04/2014

viii. Total allocation of funds (Rs): 2 070 000

ix. Total Spent (Rs):

x. Number of Research Students employed: One

xi. Postgraduate degree completed with dates: On going

xii. Number of Technical Assistants / labourers employed: None

xiii. Publications/Communications arising from the project during the reporting period:

Conference Proceedings (Full papers):

1. K.V.L. Amarasinghe, V.A. Seneviratne, L.R.A.K. Bandara, M.A.K.L. Dissanayake, "Electrical and Optical Studies on PAN-$LiBF_4$ Based Gel Polymer Electrolytes", Proceedings of the Special Session on Advanced Materials, 4th International Conference on Structural Engineering and Construction Management (ICSECM), 2013, page 118-128.

2. K.V.L. Amarasinghe, V.A. Seneviratne, L.R.A.K. Bandara and M.A.K.L. Dissanayake, "Electrical And FT-IR Study of Fumed Silica Based Gel Electrolytes; $(\text{Tetraglyme})_n\text{KI}$ And $(\text{Ethylene Glycol})_n\text{KI}$", 14th Asian Conference on Solid State Ionics (ACSSI), 2014, page 512-521.

Abstracts:

1. K.V.L. Amarasinghe, V.A. Seneviratne, L.R.A.K. Bandara, A.K. Arof and M.A.K.L. Dissanayake, "An investigation of anionic conductivity of the Composite Polymer Electrolyte based on PEO and $Pr_4N^+I^-$ salt with the filler TiO_2", Procedings of the technical sessions, International Symposium on Polymer Science and Technology 2012 in Collaboration with Industries, Institutions and Universities (IIUPST), 2012, page 31. ✓

2. K.V.L. Amarasinghe, V.A. Seneviratne, L.R.A.K. Bandara and M.A.K.L. Dissanayake, "Ionic Conductivity and FT-IR Study of Tetraglyme/KI/ Fumed Silica Gel Polymer Electrolyte", Peradeniya University International Research Session (iPURSE), 2014, page 465. ✓

3. S.H.R.T. Sooriyagoda, K.V.L. Amarasinghe, B.S. Dassanayake, V.A. Seneviratne, "Effect of Ilmenite as a Filler in the Polymer Electrolyte $(PEO)_{20}LiTf$', Peradeniya University International Research Session (iPURSE), 2014, page 448. ✓

Section 2

Executive summary of the project:

Although solid polymer electrolytes are emerging as the most suitable electrolyte material for a new generation of solid state electrochemical power sources, their practical applications have not been realized up to now due to their low room temperature ionic conductivity.

Under this research project, mainly two types of solid polymer electrolytes were studied. Those based on Polyethylene oxide (PEO) and PEO oligomers and those based on Polyacrylionitrile (PAN). Polymer electrolytes based on PEO were synthesized by common solvent casting technique or by hot pressing technique. The effect of nano-sized ceramic fillers such as Titania (TiO_2) as well as Illmenite (available in Sri Lanka) on the ionic conductivity and other properties of these electrolytes was systematically studied. Anionic conducting electrolytes were synthesized by incorporating iodide salts such as tetrapropylammonium iodide ($Pr_4N^+I^-$) or KI. Dye sensitized photoelectrochemical solar cells based on these polymer electrolytes will be fabricated and tested for their quantum efficiency.

Large cations such as Pr_4N^+, does not form strong bonds with oxygen atoms in PEO chains. The ionic conductivity of PEO-$Pr_4N^+I^-$ solid polymer electrolytes are very low and the addition of TiO_2 as a filler does not improve the iodide ion conductivity. Gel electrolytes based on PAN and $LiBF_4$ show promising conductivities, while showing strong cation-solvent and cation-anion interactions. The gel electrolytes prepared with PEO oligomer, tetraglyme, and KI show promising ionic conductivities. The dye sensitized solar cells assembled with the gel electrolytes based on tetraglyme and KI have efficiencies around 3.7%.

Section 3

i. Introduction/Background

Polymer electrolytes are the focus of intense, worldwide research and development for applications in rechargeable lithium batteries and other electrochemical devices. The technological challenge is to develop a polymer electrolyte with high room temperature ionic conductivity and mechanical properties suitable for easy, safe battery fabrication. However, the above technological advances are yet to be discovered due to the critical lack of fundamental insight into the mechanism of ion transport, which is understood only in general terms.

There are three factors that play critical roles in this mechanism: cation-anion interactions, cation-polymer interactions, and polymer segmental motion. Cation-anion interactions lead to the formation of ionically-associated species. Cation-polymer interactions occur primarily through the coordination of the cation by heteroatoms in the polymer backbone, accompanied by a change in the local conformation of the backbone. These interactions can be studied by examining the resulting structures in the polymer-salt system, in some cases using vibrational spectroscopy [10-15]. However, polymer segmental motion is a dynamic phenomenon, and inherently difficult to study directly.

It is known that the addition of ultra-fine nano-sized particles of ceramic fillers such as Al_2O_3, SiO_2 and TiO_2 [4-6] and plasticizers, is significantly improving the ionic conductivity of polymer electrolytes. The speculation for the conductivity enhancement is that the addition of ceramic fillers and plasticizers hinders the crystalline nature and increases the amorphous nature and there by increasing the segmental motion of polymers. Another possible mechanism for this conductivity enhancement is that Lewis-acid base type oxygens and OH surface groups of filler grains interact with cations and anions and provide additional sites creating favourable high conducting pathways in the vicinity of grains for the migration of ions [7,8]. However, these mechanisms are yet to be tested and verified

For fully understanding of the mechanism of ionic conductivity enhancement and there by to choose appropriate filler(s) and plasticizers for a particular polymer electrolyte system, it is essential to study them across a wide compositional range of salt – filler, salt - plasticzer and also as a function of filler type and specific surface area of grains in order to understand their conductivity behaviour and the nature of the phases present. From previous studies it is evident that the molecular weight of the polymer has also affected the ionic conductivity. In this study we have carried out extensive electrical and optical studies on PEO (poly ethylene oxide and its oligmers) or PAN based composite polymer electrolyte systems with commercially available fillers as well as naturally available fillers such as Illmenite.

Solid polymer electrolytes (SPEs) are a class of solid ionic conductors different from inorganic, glass, or ceramic electrolytes. These materials can be made by dissolving an alkali metal salt in a host polymer with a polar atom such as O, N, or S. The polymer complexes were first explained and studied by P.V. Wright and co-workers [1]. Armand *et al.* first recognized the potential applications of SPEs in electrochemical devices such as primary and secondary batteries, fuel cells, electrochromic devices or supercapacitors [2]. The previous studies have shown that the ionic conductivity of the amorphous phase above the glass transition temperature is higher than the crystalline phase of SPEs [3]. It is believed that the polymer segmental motions facilitate the ion migration in SPEs [16].

Several methods have been used to reduce the crystallinity in SPEs and enhance the conductivity through increased segmental motion. One such method is adding low molecular weight organic materials called plasticizers [4] and increase in conductivity has been observed in SPEs with plasticizers [17]. The nano-filler added systems have been studied and enhancement of ionic conductivity has been observed [4, 7, 8, 10]. Furthermore, physical parameters such as temperature, salt concentration, pressure are affecting the ionic conductivity and several studies have shown these effects.

ii. Overall and specific objectives of the proposed work

1. To synthesis polymer electrolytes with natural and commercially available fillers and plasticizers. Poly(ethylene oxide), (PEO) will be used as the polymer and molecular weights will be chosen from low to high values.
2. To synthesis electrolytes with PEO oligomers and fillers.
3. To measure the ionic conductivity of polymer electrolytes with natural and commercially available fillers/plasticizers and electrolytes with PEO oligomers and fillers using AC impedance techniques.
4. To measure the temperatures of thermal transitions of the above electrolytes.
5. To identify the phases present in the polymer electrolytes.

iii. Materials and methods

(I) Materials and sample preparation methods

1. PEO based solid polymer electrolyte systems

Polyethylene oxide (PEO, Mw 4x10^6, Aldrich), tetrapropylammonium iodide ($Pr_4N^+I^-$) (98 %, Aldrich), lithium triflate (LiTf) (98 %, Aldrich), iodine (Fluka), glacial acetic acid (99%, Fisher scientific), Triton-X (Aldrich), ethanol (BDH) were used as received. Fluorine-doped tin oxide glass plates (FTO) were used as a substrate for coating TiO_2 paste. Ruthenium dye (N719) (di-tetrabutylammoniumcisbis(isothiocyanato) bis(2,2′-bipyridyl-4,4′ dicarboxylicacid) was used as the sensitizer. Prior to use PEO, $Pr_4N^+I^-$, LiTf, TiO_2 and Ilmenitewere vacuum dried at 50 °C, 80 °C, 120 °C, 100 °C and 180 °C for 24 hours prior to use.

PEO and $Pr_4N^+I^-$ based electrolyte system

Sample preparation

First a series of filler free SPEs with different O: I ratios (5, 10, 20, 30, 40, 50, 60, 80 and 90) were prepared by solvent casting technique. After that the filler was added to a selected composition as a percentage of the total weight of PEO and $Pr_4N^+I^-$.

Sample preparation for Dye Sensitized Solar Cell

For this study O: I ratio was selected as 60:1 as it showed a relatively high anionic conductivity among the samples with low salt concentrations. The desired amount of PEO (0.25 g) and $Pr_4N^+I^-$(0.0296 g) were dissolved in anhydrous acetonitrile using magnetic stirring at room temperature for 24 hours in order to obtain homogeneous viscous slurry. Then the slurry was casted on to a Teflon plate and allowed it to air dry at room temperature for 24 hours in order to gradually evaporate the solvent. This solvent casting method was yielded visually homogeneous PE films which were vacuum dried at room temperature for 24 hours prior to use for measurements. After that the filler TiO_2 was added to the composition as a percentage of the total weight of PEO and $Pr_4N^+I^-$. For Dye Sensitized Solar Cells the polymer electrolyte samples were prepared with Iodine (I_2). The mole amount of the I_2 was taken to be one tenth of the mole amount of the iodide salt.

Solar cell Fabrication

Preparation of TiO_2 colloidal particles

First 20 ml of Tetraisopropoxide (TiP) was taken. Then 2.5 ml of acetic acid and 25 ml of ethanol were added. After that the steam was allowed to pass through the solution. Finally 50 ml water was added to the solution and it was autoclaved at 150 ^{0}C for 3 hours.

Preparation of Photo- electrode

The TiO_2 starting solution was prepared as follows. First 20 ml of autoclaved TiO_2 colloidal was taken and 5.5 ml of acetic acid was added to it and was grinded well using motor. Then 5 drops of triton x100 was added and mixed well. Finally 20 ml of ethanol was added to the solution. Then the solution mixture was sprayed onto heated (150 °C) FTO glass substrate and subsequently sintered in air at 500 °C for 30 min. The TiO_2 electrode, pre-heated to 80 °C, was immersed in a mixture of 50 ml of acetonitrile and 50 ml of t-butanol (volume 1:1) containing 60 mg of Ruthenium dye N719 for 24 hours.

PEO and LiTf based solid electrolyte system

Sample preparation

For this study, a series of filler free SPEs with different O: I ratios were prepared by solvent casting technique.. The desired amount of PEO (0.5 g) and LiTf were dissolved in anhydrous acetonitrile using magnetic stirring at room temperature for 24 hours in order to obtain homogeneous viscous slurry. Then the slurry was casted on to a Teflon plate and allowed it to air dry at room temperature for 24 hours in order to gradually evaporate the solvent. This solvent casting method was yielded visually homogeneous PE films which were vacuum dried at room temperature for 24 hours prior to use for measurements. After that the filler was added to a selected composition as a percentage of the total weight of PEO and LiTf.

2. *PAN and $LiBF_4$ based gel polymer electrolyte system*

Polyacrylonitrile (PAN) (average M_w 150,000), lithium tetrafluoroborate ($LiBF_4$) (98%), ethylene carbonate (EC) (98%), propylene carbonate (PC) and TiO_2 (99.9%) were purchased from Aldrich and used as starting materials. Prior to use EC, $LiBF_4$ and TiO_2 were vacuum dried at room temperature, 60 °C and 100 °C respectively.

Preparation of gel polymer electrolyte

The required amounts of $LiBF_4$, EC and PC were dissolved with the aid of magnetic stirring for half an hour until the salt is completely dissolved. Then PAN was added to the solution and the mixture was heated at 140°C while magnetically stirring for one hour. The resulting homogeneous viscous solution was casted on to apetry dish. After cooling, a transparent polymer electrolyte could be obtained. The filler was added as a percentage of the weight of (polymer + salt).

Battery fabrication

Cathode preparation

$LiMn_2O_4$ was used as the cathode active material. 80 wt% of $LiMn_2O_4$, 10 wt% of carbon black and 10 wt% of poly(vinyldine fluoride) were dissolved in anhydrous acetonitrile. Then the solution was air dried at room temperature until the solvent was evaporated. Then the pellets were prepared using Paul Weber press machine and sintered at 180 °C for 1 hour under vacuum.

Anode preparation

Natural graphite was used as the anode. 88wt % of graphite, 10wt% of carbon black and 10wt% of poly(vinyldine fluoride) were dissolved in anhydrous acetonitrile. Then the solution was air dried at room temperature until the solvent was evaporated. Then the pellets were prepared using the Paul Weber press machine and sintered at 180 °C for 1 hour under vacuum.

The cell was assembled in a home made cell holder. The configuration of the cell was $LiMn_2O_4$/GPE/Graphite.

3. *Tetraglyme and KI system with fumed SiO_2*

Tetraglyme (Aldrich), potassium iodide (KI) and fumed silica (SiO_2) (Aldrich) were used as the starting materials. Prior to use, SiO_2 was heated at 500 °C for 24 hours and KI was heated at 120 °C under vacuum for 24 hours.

Sample preparation

First a series of liquid electrolytes were prepared by mixing tetraglyme and KI, at an ether oxygen to salt ratios of 12:1, 15:1, 20:1, 25:1, 30:1, 40:1, 50:1, 60:1 and 80:1. The composite gel was then formed by adding the appropriate amount of fumed silica to achieve a filler concentration of 10wt %.

Solar cell Fabrication

Photo- electrode preparation

The TiO_2 starting solution was prepared as follows. First 20 ml of autoclaved TiO_2 colloidal was taken and 5.5 ml of acetic acid was added to it and was grinded well using motor. Then 5 drops of triton x100 was added and mixed well. Finally 20 ml of ethanol was added to the solution. Then the solution mixture was sprayed onto heated (150 °C) FTO glass substrate and subsequently sintered in air at 500 °C for 30 min.The TiO_2 electrode, pre-heated to 80 °C, was immersed in a mixture of 50 ml of acetonitrile and 50 ml of t-butanol (volume 1:1) containing 60 mg of Ruthenium dye N719 for 24 hours.An active cell area was 0.25 cm^2.

(II) Characterization Techniques

1. *Conductivity measurements*

The complex impedance spectroscopy measurements were performed using the computer controlled solatron SI-1260 impedance analyzer in the frequency range 20 Hz - 10 MHz. For SPEs the conductivity was studied in the temperature range 25 °C to 85 °C and for GPEs, the studied temperature range was 25 °C to 65 °C. A disk shaped SPE sample with the thickness 100 – 400 μm was sandwiched between two stainless electrodes with the diameter 13 mm to measure the complex impedance spectroscopy. For liquid electrolytes a home made glass sample holder was used for complex impedance spectroscopy.

2. *DSC measurements*

The melting temperatures and melting enthalpies of PEO and $Pr_4N^+I^-$ SPE system, were investigated using the Perkin Elmer Pyris 1 DSC with a rate of 5 °C min^{-1}. The samples were heated from 25 °C to 80 °C. Then they were again cooled to 25 °C. This was repeated twice for each sample.

3. *DC polarizing measurements*

In order to investigate the ionic nature of the SPE, GPE and liquid electrolyte samples, the DC polarizing test was done. A DC voltage of 1 V was applied to the filler free and filler added samples which were sandwiched between two polished stainless steel electrodes according to the SS/Sample/SS configuration, to measure the DC current through the samples with the time, using a Keithley model 485 AutorangingPicoammeter.

4. *Fourier Transform Infrared Spectroscopy (FTIR)*

FTIR for SPE, GPE and liquid electrolyte samples were done using Nicolet IS10 FTIR spectrometer with a 4 nm resolution.

5. *X-Ray Diffraction Technique (XRD)*

Both filler free and filler added samples of PEO based SPE systems were examined by the Siemens X-ray diffractometer (D 5000) with step size 0.02^{o},in the 2θ diffraction angle range from 3^{o} to 80^{o}.

6. *Spherulites*

The spherulite growth of the filler free and filler added samples of PEO based SPE systems were studied using the pictures taken by Euromex Holland polarized light microscope.

7. *Solar cell characterization*

The solid polymer electrolyte based Dye sensitized solar cells (DSSC) were fabricated by sandwiching the electrolyte film in between Platinum (Pt) coated FTO electrode and dye absorbed TiO_2 electrode with configuration Glass / FTO / TiO_2 / Dye / solid electrolyte /Pt / FTO / Glass . The photocurrent–voltage (I–V) characteristics of the cells were measured under the illumination of Portable solar simulator Peccell (PEC-L01) using a computer controlled setup coupled to a Keithley 2400 Source meter.

8. *Battery characterization*

The cells were subjected to 5 mA charge-discharge current at room temperature using the Maccor Battery tester. The upper voltage limit was 4.2 V and the lower voltage limit was 0.5 V.

iv. Results and Discussion

System 1. PEO and $Pr_4N^+I^-$ based polymer electrolytes and TiO_2 added composite polymer electrolytes

Conductivity measurements

The polymer electrolytes $(PEO)_nPr_4N^+I^-$ (n= 5, 10, 20, 30, 40, 50, 60, 80 and 90) were prepared using poly(ethylene) oxide and the salt tetrapropylammonium iodide ($Pr_4N^+I^-$) by using the solvent casting method.

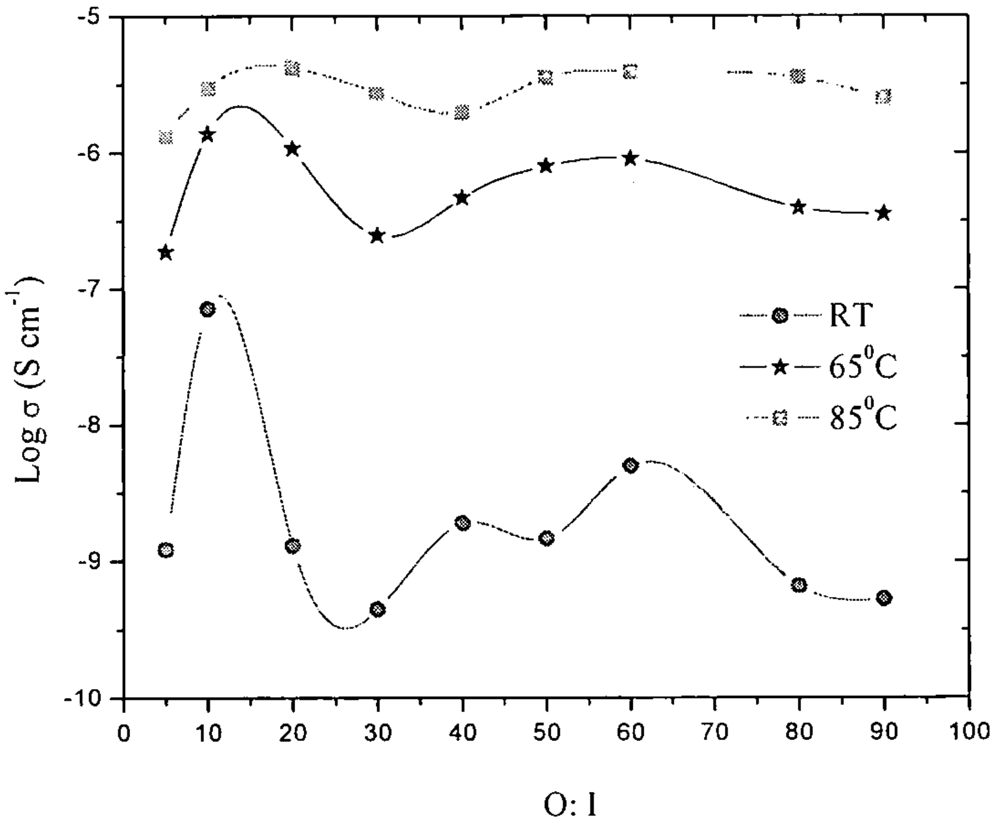


Figure 01: The graph of Log (conductivity) vs. 0:I ratio for $(PEO)_n$ $Pr_4N^+I^-$ (n= 5, 10, 20, 30, 40, 50, 60, 80 and 90) at room temperature, 65°C and 85°C.

The conductivities of PEO-$Pr_4N^+I^-$ electrolytes are low compared to PEO-Li salt electrolytes. The polymer electrolytes of $(PEO)_{10}Pr_4N^+I^-$ and $(PEO)_{60}Pr_4N^+I^-$ were shown high conductivities compared to the other concentrations, while the 10:1 sample having the highest conductivity. The 60:1 sample, $(PEO)_{60}Pr_4N^+I^-$, was chosen to study the effect of the filler on conductivity. The 60:1 sample has a relatively low salt concentration and slightly higher conductivity compared to other samples having low salt concentrations. The intension is to study the effect of the filler on the anion conductivity and a high salt concentration is not suitable because the effect of the filler may not be dominant.

The filler was added as 10% from the weight of the polymer electrolytes to the samples $(PEO)_nPr_4N^+I^-$ (n = 30, 40, 50, 60, 80 and 90). As shown in the Figure 02 $(PEO)_{50}Pr_4N^+I^-$ shows the highest conductivity. So that the $(PEO)_{50}Pr_4N^+I^-$polymer electrolyte was also chosen to add the filler in different percentages and to study further.

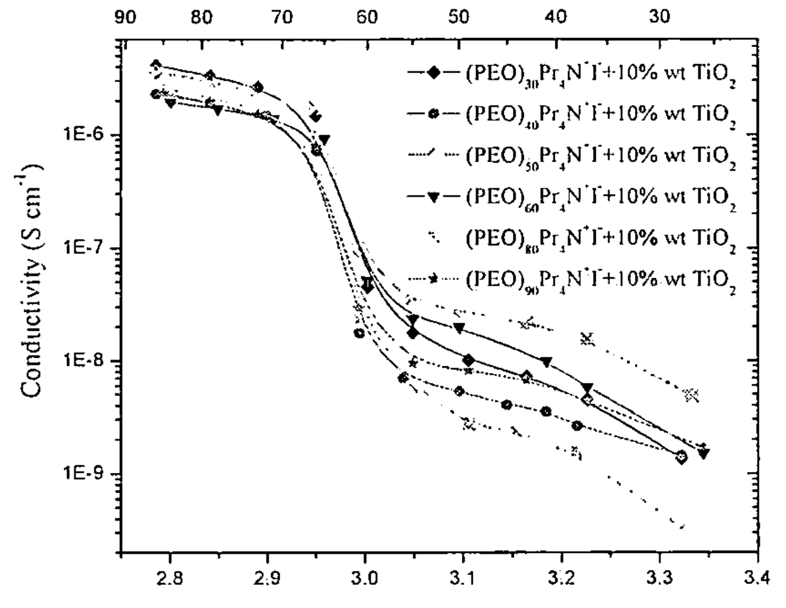


Figure 02: The graph of conductivity vs. 1000/T of $(PEO)_nPr_4N^+I^-$ + 10% wt TiO_2 (n= 30, 40, 50, 60, 80 and 90).

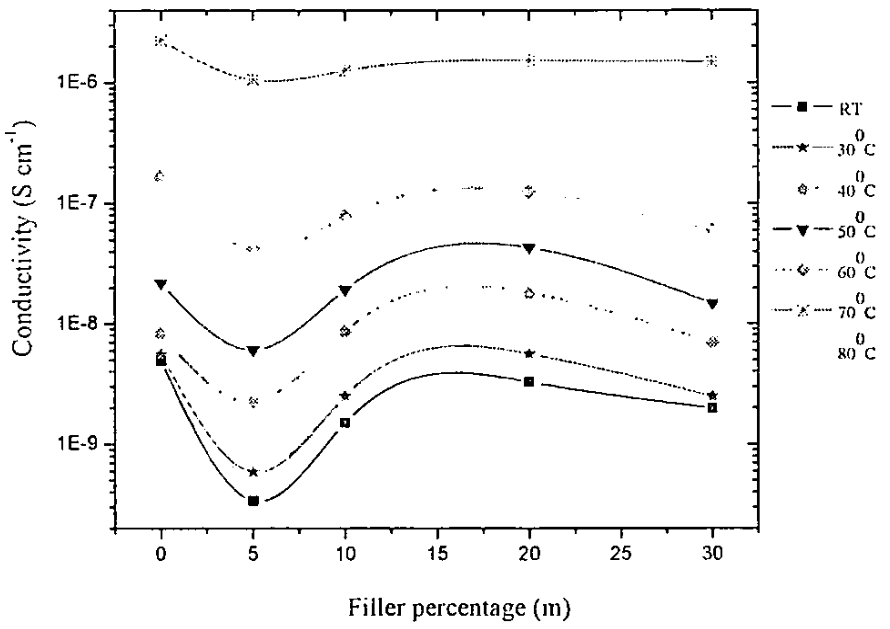


Figure 03: The conductivity variation of the $(PEO)_{60}Pr_4N^+I^-$ + m% wt TiO_2 (m = 0, 5, 10, 20 and 30)

Then the filler was added to $(PEO)_{60}Pr_4N^+I^-$ as 5%, 10%, 20% and 30% of the total weight of the polymer electrolyte $(PEO)_{60}Pr_4NI$. The Figure 03 shows the isothermal variation of the conductivity of the filler added electrolytes.

The Figure 04 shows the conductivity variation of the filler added samples of $(PEO)_{50}Pr_4N^+I^-$.

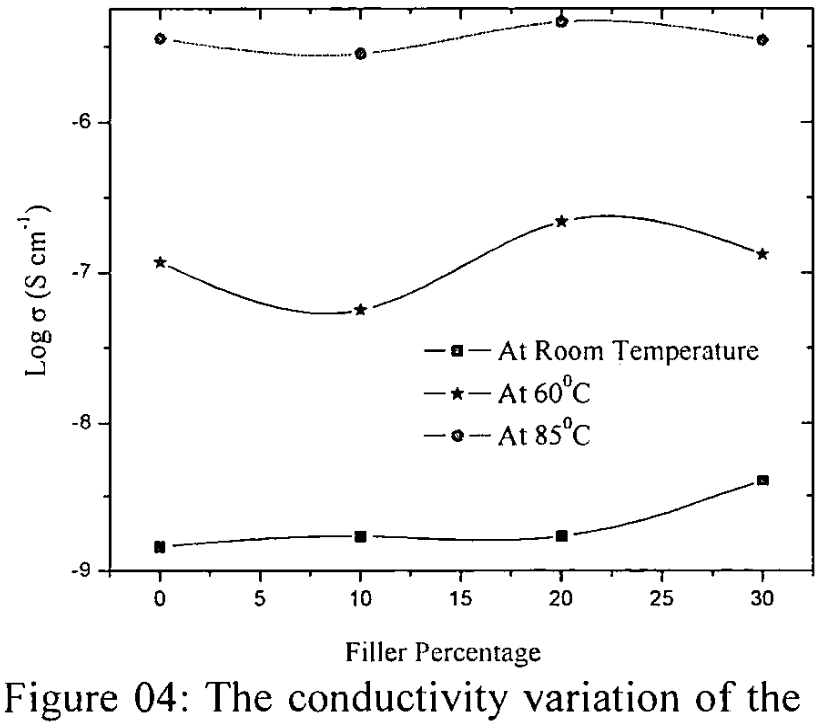


Figure 04: The conductivity variation of the $(PEO)_{50}$ $Pr_4N^+I^-$ + m% wt TiO_2 (m = 0, 10, 20 and 30).

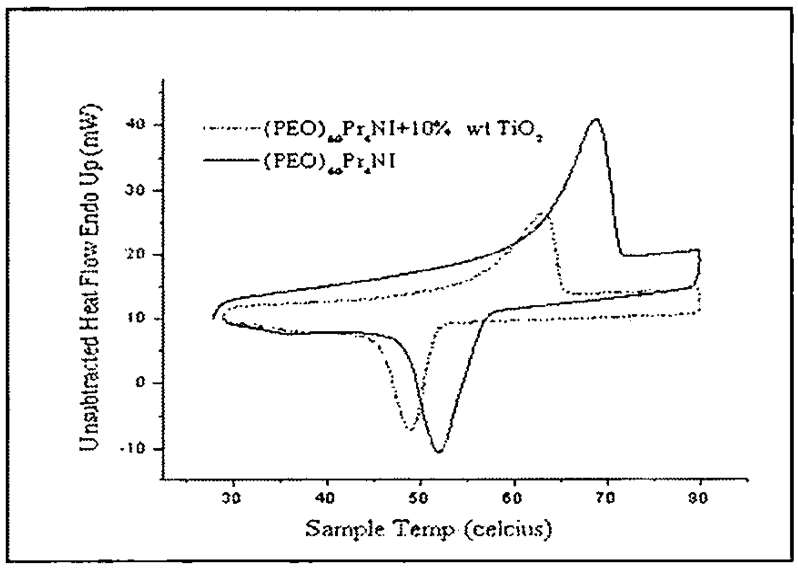


Figure 05: The DSC curves of $(PEO)_{60}Pr_4NI$ and $(PEO)_{60}Pr_4NI$ + 10% wt TiO_2 polymer electrolytes.

From Figures 03 and 04, it is evident that the addition of the filler has not enhanced the ionic conductivity of PEO-$Pr_4N^+I^-$system. Enhancement in ionic conductivities can be observed when fillers with high dielectric constants are added to PEO-Li salt systems. The enhancement of the conductivity is believed to be due to two mechanisms.

1. Addition of filler decreases the pure PEO melting temperature and glass transition temperature, which means that the amorphous nature of the sample has been increased. Then the segmental motions of the polymer are increased. The Li ion migration is via segmental motions of the polymer chain and therefore the ionic conductivity is increased due to the addition of filler
2. The second mechanism is believed to be due to the additional pathways opened through the surface groups of the filler particles.

However, in the $(PEO)_nPr_4N^+I^-$system, there is no enhancement in the ionic conductivity due to the addition of filler TiO_2. The mobile ionic species in this system is I^- and the cation, Pr_4N^+, is bulk and immobile. The cation is coordinating with the oxygen atoms in the polymer chain and I^- is moving with no coordination to the polymer chain. Therefore, increase in the segmental motions cannot be directly influencing the I^- conductivity.

DSC data

Figure 05 shows the DSC (Differential Scanning Calorimetry) curves for $(PEO)_{60}Pr_4N^+I^-$and $(PEO)_{60}Pr_4N^+I^-$ + 10% wt TiO_2 polymer electrolytes. The addition of the filler has been decreased the melting temperature and the enthalpy of melting the pure PEO regions in the polymer electrolyte.

Table 01: The melting temperatures and the enthalpies of pure PEO and $(PEO)_{60}Pr_4N^+I^-$ + n% wt TiO_2SPEs, where n= 0, 5, 10, 15, and 20.

Polymer Electrolyte	*ΔH_m(J/g)*		*T_m (^oC)*
	1st heating	**2nd heating**	
Pure PEO	152.058	94.323	65.098
$(PEO)_{60}Pr_4N^+I^-$	108.576	83.78	64.701
$(PEO)_{60}Pr_4N^+I^-$ + 5%wt TiO_2	108.472	83.891	64.716
$(PEO)_{60}Pr_4N^+I^-$ + 10%wt TiO_2	100.69	80.408	64.654
$(PEO)_{60}Pr_4N^+I^-$ + 15%wt TiO_2	93.932	79.657	63.685
$(PEO)_{60}Pr_4N^+I^-$ + 20%wt TiO_2	93.179	72.306	64.452

The reduction in melting temperature and the enthalpy of melting shows the reduction of the crystallinity of the sample. Unlike in a Li ion conductor this slight reduction of crystalline nature is not facilitating the I^- ion movement, because the I^- ion movement is not facilitated by the segmental motion.

The optical micrographs

The optical micrographs obtained from the polarized light microscope (PLM) are shown in the Figure (06).

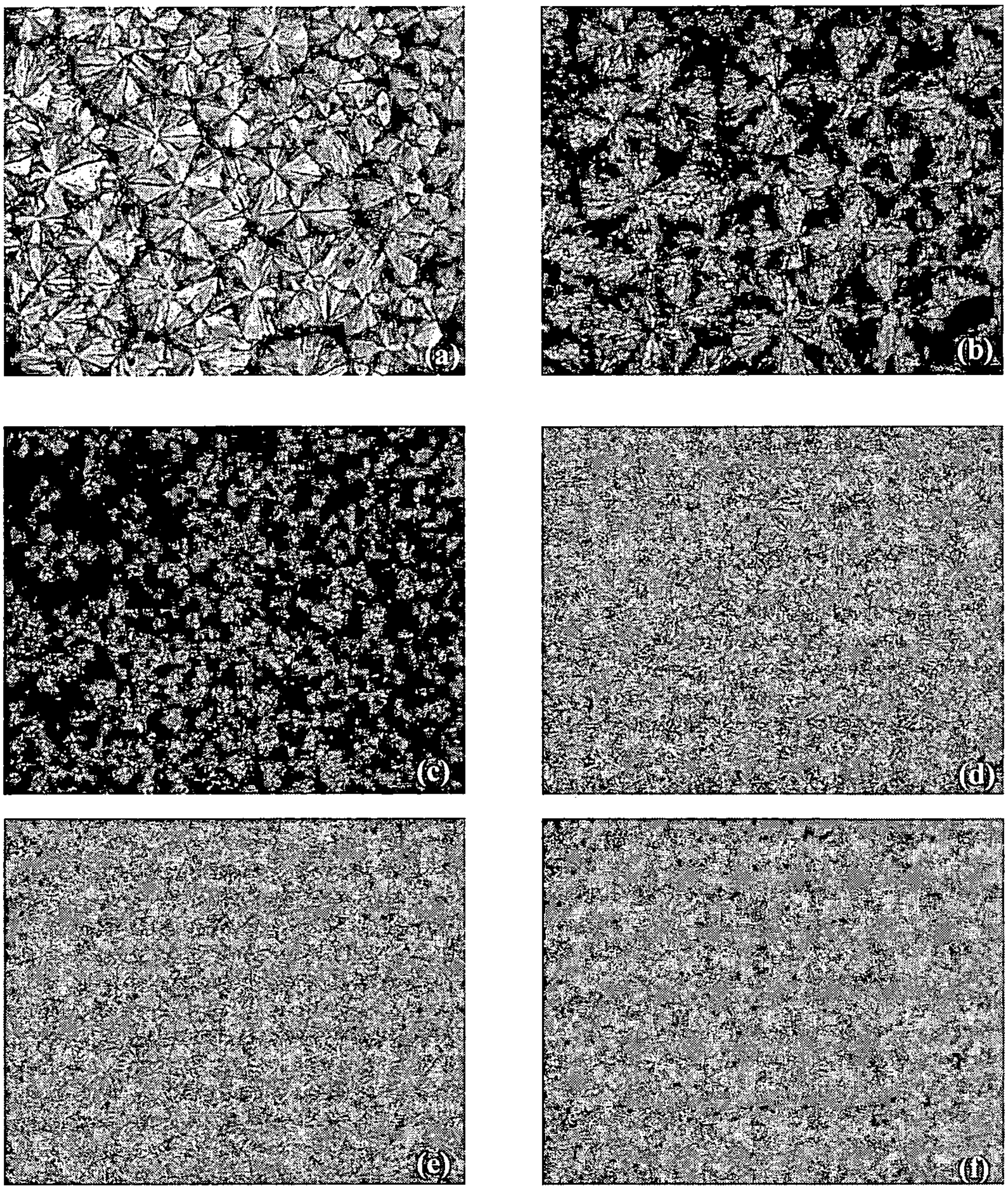


Figure (06): The spherulites formation of the $(PEO)_{60}Pr_4N^+I^-$ (a), $(PEO)_{60}Pr_4N^+I^-$ + 5%wt TiO_2 (b), $(PEO)_{60}Pr_4N^+I^-$ + 10%wt TiO_2 (c), $(PEO)_{60}Pr_4N^+I^-$+15%wt TiO_2 (d), $(PEO)_{60}Pr_4N^+I^-$ + 20%wt TiO_2 (e) and $(PEO)_{60}Pr_4N^+I^-$ + 30%wt TiO_2 (f).

Spherulites have semi crystalline structure where highly ordered lamellae plates are interrupted by amorphousregions. Formation of spherulite is associated with the crystallization of the PE, so that it can affect the crystallinity of the PE. The optical micrographs shown in the Figure (06) showing a reduction in the spherulite size as the filler added. It is evident that the addition of the filler has been decrease the crystalline nature of the PE while increasing its amorphous nature. Since the ion conductor of the PEO-$Pr_4N^+I^-$ system is I^- and it is not coordinating with the polymer backbone, this increment of the amorphous nature does not enhance the ionic conductivity of the system.

Conductivity measurements of the PEs for DSSCs

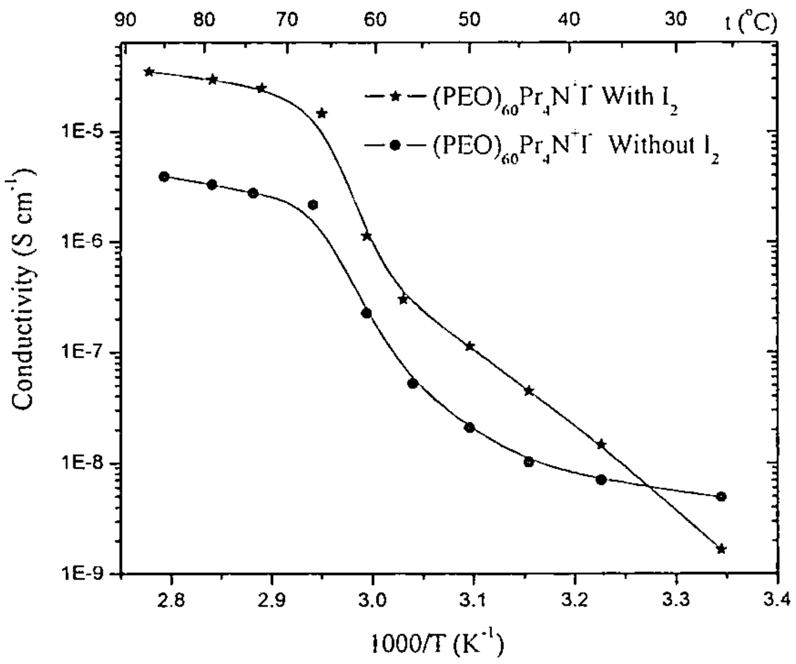


Figure (07): The conductivity variation of the $(PEO)_{60}Pr_4N^+I^-$ with and without I_2.

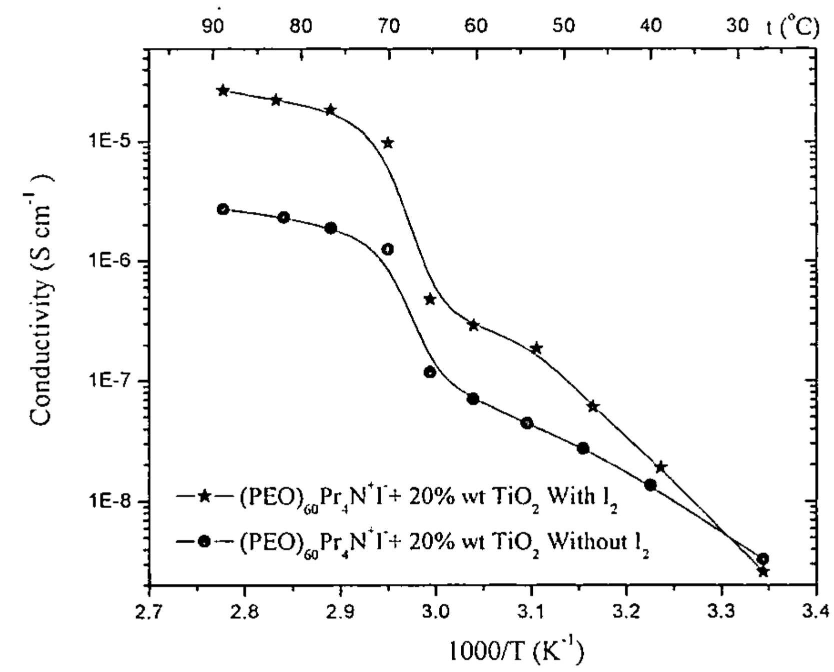


Figure (08): The conductivity variation of the $(PEO)_{60}Pr_4N^+I^-$ + 20% wt TiO_2 with and without I_2.

The room temperature conductivities of $(PEO)_{60}Pr_4N^+I^-$ with and without I_2 were 1.65×10^{-9} S cm^{-1} and 4.93×10^{-9} S cm^{-1} respectively. At 80 °C the anionic conductivities of $(PEO)_{60}Pr_4N^+I^-$ with and without I_2 were 3.52×10^{-5} S cm^{-1} and 3.31×10^{-6} S cm^{-1} respectively.

The room temperature conductivities of $(PEO)_{60}Pr_4N^+I^-$+ 20% wt TiO_2 with and without I_2 were2.57×10^{-9} S cm^{-1} and 3.26×10^{-9} S cm^{-1} respectively. At 80 °C the anionic conductivities of $(PEO)_{60}Pr_4N^+I^-$with and without I_2 were 2.23×10^{-5} S cm^{-1} and 2.32×10^{-6} S cm^{-1} respectively.

Solar cell characterization

Table 02: Solar cells parameters of the DSSCs for $(PEO)_{60}Pr_4N^+I^-$ and$(PEO)_{60}Pr_4$ N^+I^- + 20% wt TiO_2.

Polymer Electrolyte	J_{sc} *(mA cm^{-2})*	I_{sc} *(mA)*	*Efficiency (%)*	*Fill Factor*	V_{oc} *(mV)*
$(PEO)_{60}Pr_4N^+I^-$	**3.39**	**0.848**	**1.37**	**0.55**	**737**
$(PEO)_{60}Pr_4N^+I^-$ + 20% wt TiO_2	**3.63**	**0.907**	**1.77**	**0.63**	**782**

Although this polymer electrolyte is a fully anionic conductor, the low ionic conductivities have led to low quantum efficiencies.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR for both filler free and filler added samples were done using Nicolet IS10 FTIR spectrometer with a 4 nm resolution.

Generally in PEO-salt complexes, the cation is coordinating with the ether oxygen of the polymer backbone. The cation is moving by breaking one or more metal-oxygen bonds and then replacing these bonds by links to oxygen, while anion moves freely through the complex. These interactions may influence the local structure of the polymer backbone. These changes of the local structure can be clearly seen by the FIR spectra.

If the cations were coordinated with the ether oxygen of PEO, changes in the ether oxygen vibrational modes, such as C-O-C asymmetric and symmetric stretching modes, and deformation modes in the range of 900–1200 cm^{-1} can be expected. The strong band at ~1110 cm^{-1} is representing the C-O-C stretching mode, which has shoulders at 1060 $cm^{-1}$and 1149 cm^{-1}. The band become broader as the salt concentration increased, while the peak positions remain same.

The strong peaks appeared at 842, 1241, 1341, 1360 cm^{-1} are attributed to modes in the crystalline phase of PEO. The weak band appears at 948 cm^{-1} infrared active band for PEO in the amorphous phase. This shows the addition of the salt $Pr_4N^+I^-$ doesn't change the crystalline nature of the complex significantly.

The most prominent peak of C–O–C symmetric stretching mode appears at 1110 cm^{-1}. The presence of the crystalline phase is confirmed by the appearances of triplet maxima of C–O–C stretching vibrations at ~ 1147, 1110 and 1060 cm^{-1}in the pure PEO. The width of the peak at 1110 $cm^{-1}$is increasing with the salt concentration. This broadening clearly indicates Pr_4N^+ ion coordination with ether oxygen of PEO.

The position of theC–O–C symmetric stretching mode (1110–1113 cm^{-1}) does not differ with TiO_2content. The width of the C–O–C symmetric stretching mode has been increased as the salt is added to PEO and then it has been decreased with the addition of the filler TiO_2. The grain boundary effect of TiO_2may be the reason for the changes of the spectra for 25% TiO_2. Lewis acid centres on the surface of TiO_2interact with the base oxygen of polyether chain. This acid–base interaction increases the gauche conform of PEO chain. With further increase of TiO_2content, the width of the C–O–C symmetric stretching band has been slightly increased. Both Ti^{4+} and Pr_4N^+cations are competing against each other to coordinate with ether oxygen. The increase of the band in the 25 wt.% suggests that Ti^{4+}interacts with ether oxygen of solvating Pr_4N^+.

System 2. PEO and LiTf based solid polymer electrolyte system with TiO_2 and Ilmenite as fillers

DC polarizing measurements

In order to investigate the ionic nature of the filler free and filler added samples the DC polarizing test was done. A DC voltage of 1 V was applied to the filler free and filler added samples which were sandwiched between two polished stainless steel electrodes according to the SS/Sample/SS configuration, to measure the DC current through the samples with the time, using a Keithley model 485 AutorangingPicoammeter.

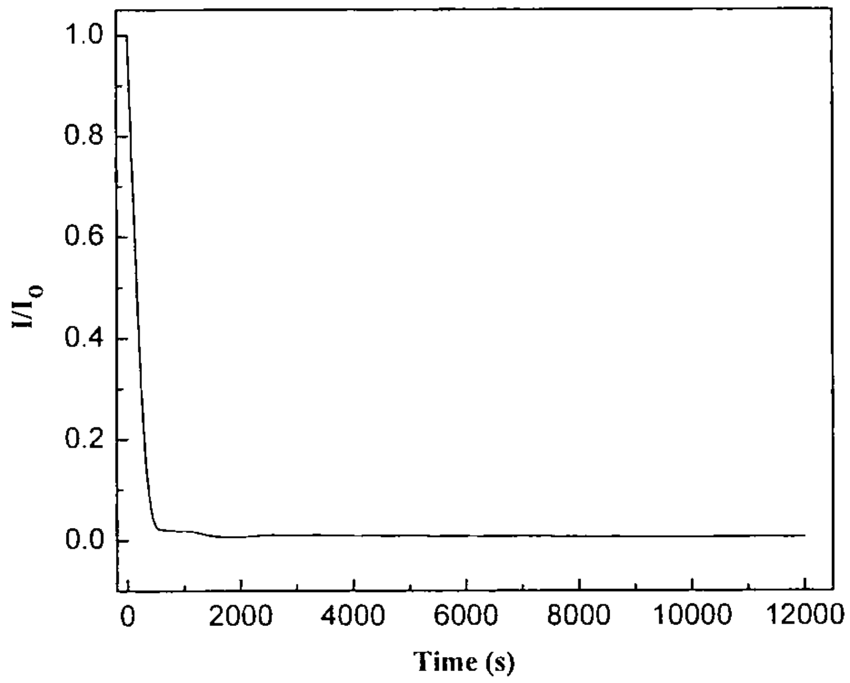


Figure 09: The DC current variation as a function of time of SPE $(PEO)_{20}LiTf$+ 10% wt Ilmenite

The DC polarizing data extract the contribution of the ions rather than electrons to the conductivity. All the filler free and filler added samples prepared were predominantly ionic conductors and the electronic conductivity is negligible.

Conductivity measurements

The AC complex impedance measurements were performed using the computer controlled solatron SI-1260 impedance analyzer in the frequency range 20 Hz - 10 MHz and in the temperature range 25 °C to 85 °C. A disk shaped electrolyte sample with the thickness 100 – 300 µm was sandwiched between two stainless electrodes with the diameter 13 mm to measure the AC complex impedance.

As shown in the Figure 10 SPE with 10:1 composition exhibits the highest conductivity. However to investigate the filler effect, 20:1 composition was chosen due to it's relatively high ionic conductivity and less amorphous nature compared to the 10:1 composition.

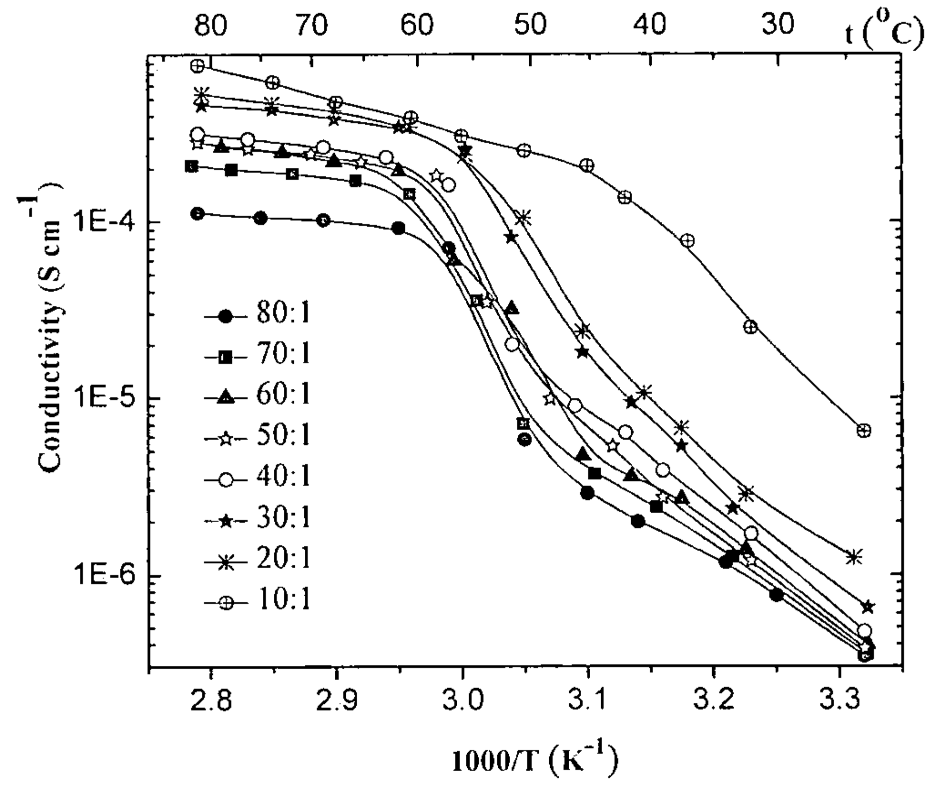


Figure 10: The ionic conductivity variation as a function of temperature of SPE $(PEO)_nLiTf$ (n= 10, 20, 30, 40, 50, 60, 70 and 80)

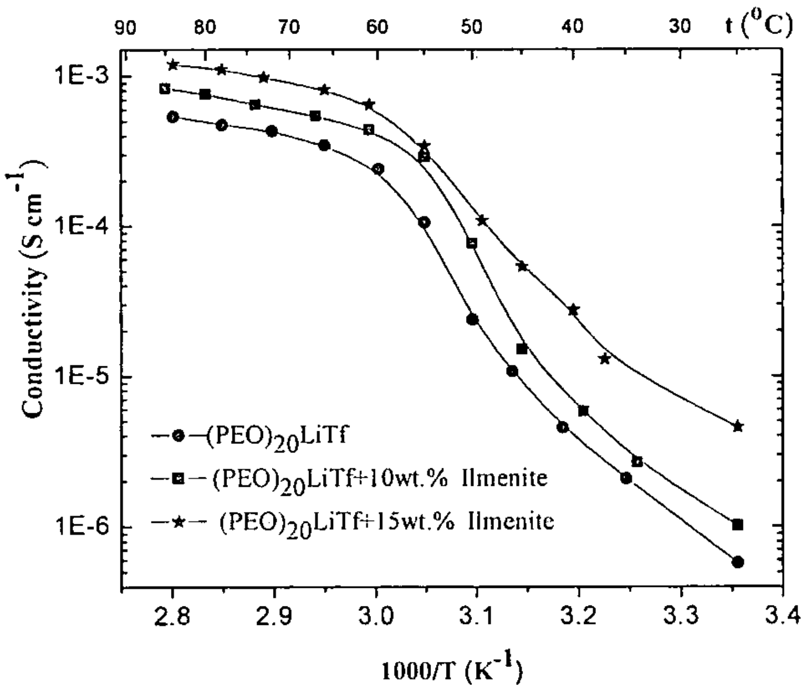


Figure 11: The ionic conductivity variation as a function of temperature of SPE $(PEO)_{20}LiTf$ with filler Ilmenite.

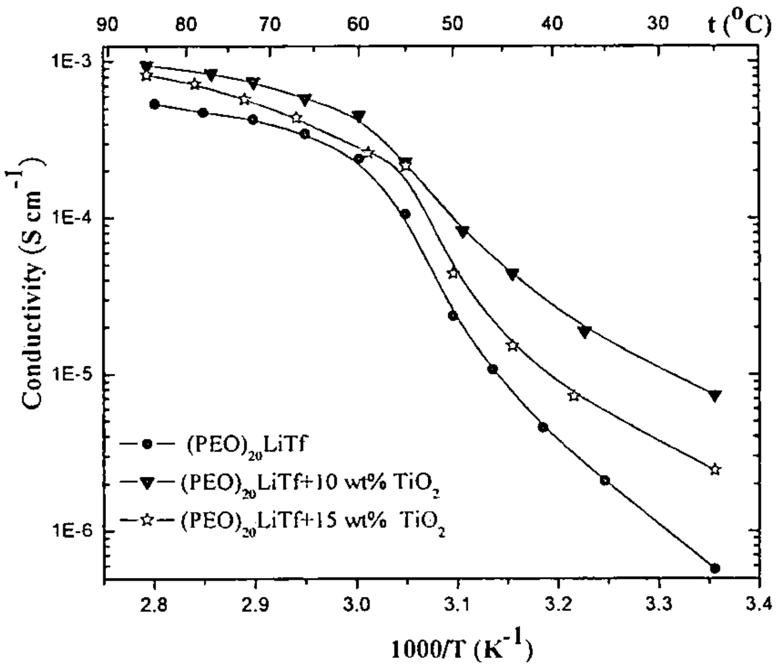


Figure 12: The ionic conductivity variation as a function of temperature of SPE $(PEO)_{20}LiTf$ with filler TiO_2

As seen in the figure 11, addition of 15% of the filler Ilmenite has been enhancing the ionic conductivity. The filler titania was added the same composition 20:1 to compare the filler effect of titania and Ilmenite.Figure 12 depict the ionic conductivity variation of the TiO_2 added SPEs of the $(PEO)_{20}LiTf$. The highest conductivity has been showed with the addition of 10% wt of the filler TiO_2.

The optical micrographs

The spherulite growth of the filler free and filler added samples were studied using the pictures taken by Euromex Holland polarized light microscope. The optical micrographs obtained from the polarized light microscope (PLM) are shown in the Figure 13.

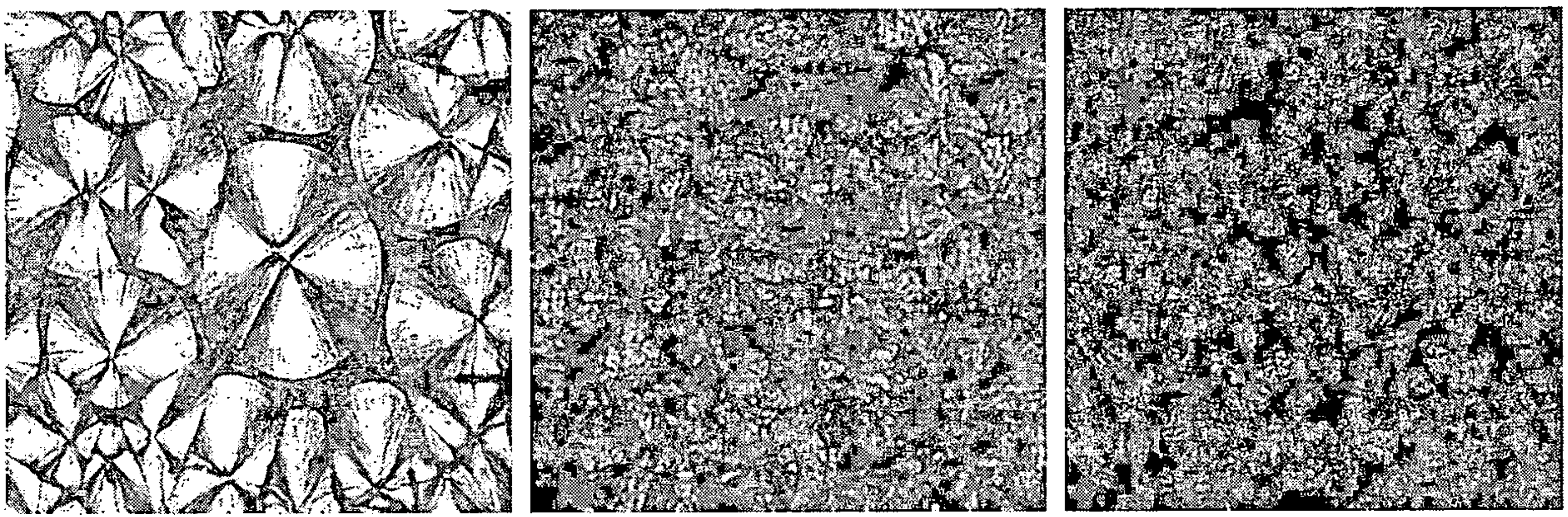

(a) (b) (c)

Figure 13: The spherulites formation of the $(PEO)_{20}LiTf$(a), $(PEO)_{20}LiTf$+ 10%wt TiO_2 (b) and $(PEO)_{20}LiTf$+ 15%wt Ilmenite (c)

The optical micrographs shown in the Figure 13showing a reduction in the spherulite size as the filler TiO_2 and Ilmenite added. It is evident that the addition of the filler has been decrease the crystalline nature of the PE while increasing its amorphous nature.

XRD data

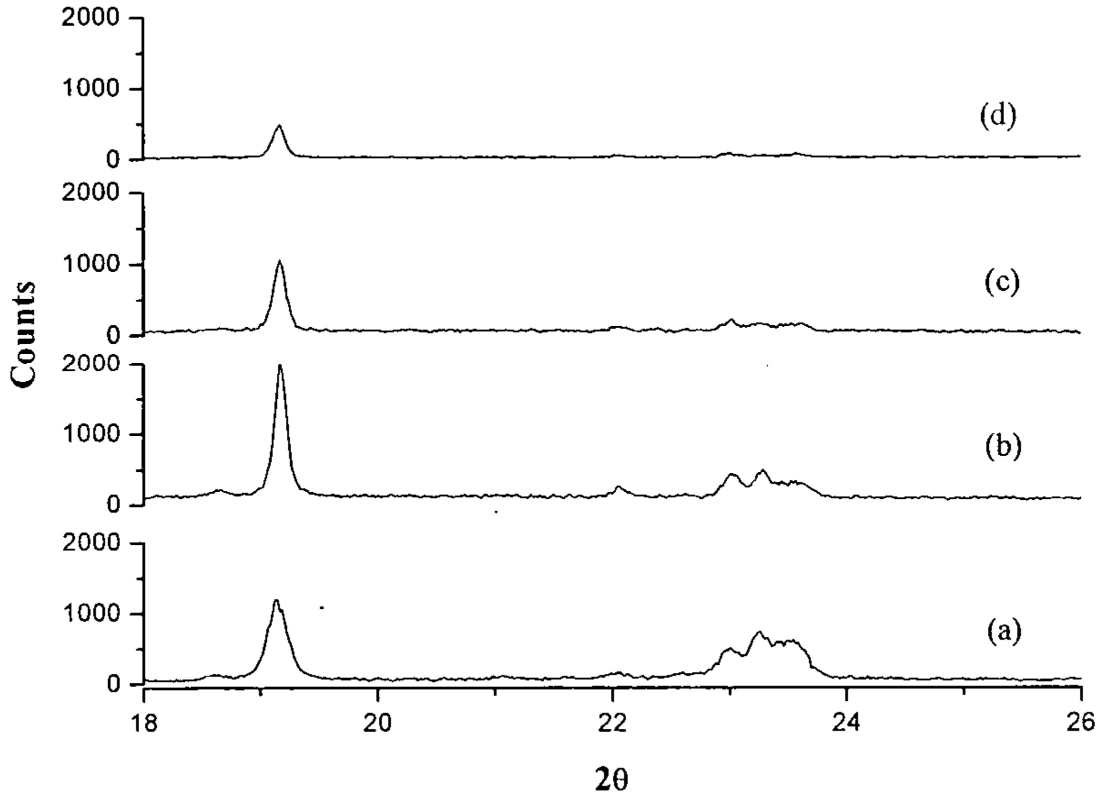


Figure 14: The spherulites formation of the pure PEO(a), $(PEO)_{20}LiTf$(b), $(PEO)_{20}LiTf$+ 10%wt Ilmenite (c) and $(PEO)_{20}LiTf$+ 15%wt Ilmenite (d)

Figure 14 showing the XRD spectra of Pure PEO and SPEs. The characteristic crystalline peaks of PEO are observed at 19° and 23°which are assigned to (120) and (112) respectively. This graph clearly shows that intensity of the PEO peaks decreases and broad spectrum disappears after addition of Ilmenite. The presence of 15% Ilmenite has reduced the intensity of crystalline peaks significantly. This suggests that amorphous nature of the SPEs has increased after addition of Ilmenite.

System 3. PAN and $LiBF_4$ based gel polymer electrolyte system

Conductivity data

Table 03: Compositions of the electrolytes prepared by varying PAN, $LiBF_4$, EC and PC

	Composition	**EC (g)**	**PC (g)**	**PAN (g)**	**$LiBF_4$ (g)**	**σ (10^{-3} × S cm^{-1})**
System I	*a*	0.40	0.40	0.05	0.15	4.25
	b	0.40	0.40	0.10	0.10	3.88
	c	0.40	0.40	0.15	0.05	3.10
System II	*d*	0.35	0.35	0.05	0.25	2.32
	e	0.35	0.35	0.10	0.20	1.33
	f	0.35	0.35	0.15	0.15	0.98
	g	0.35	0.35	0.20	0.10	0.58

The room temperature ionic conductivity values of GPE with different compositions are listed in Table 03.

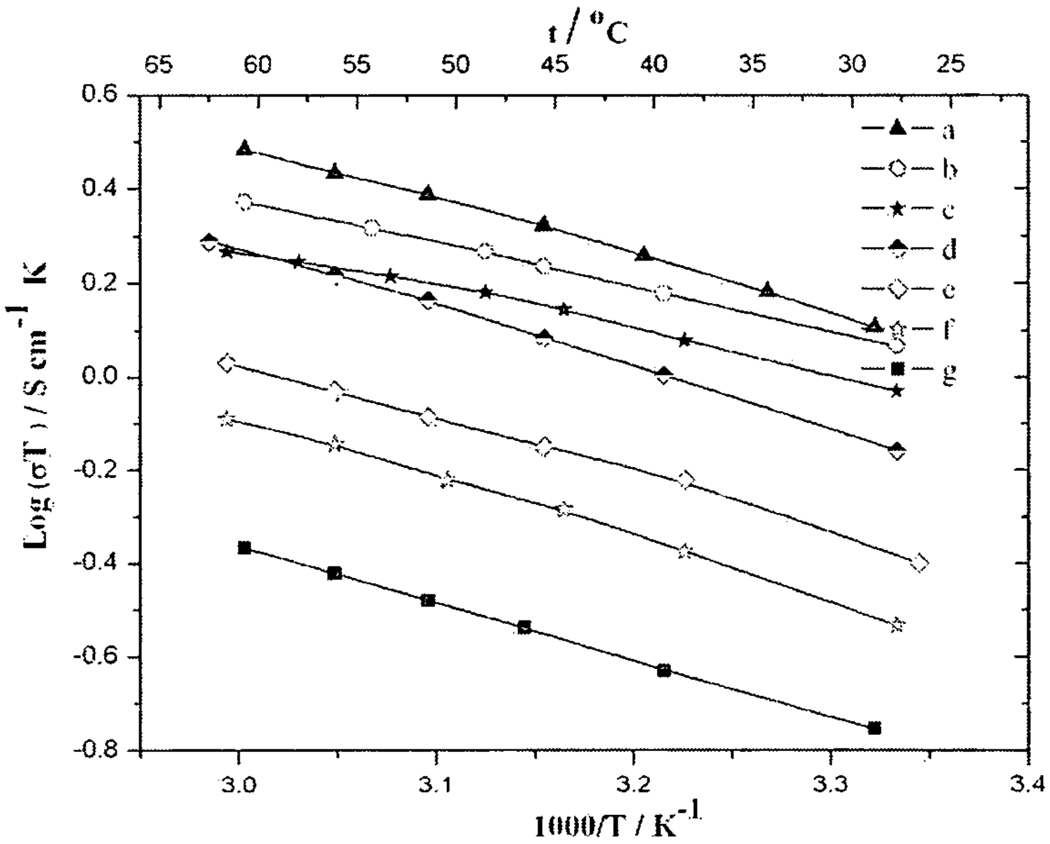
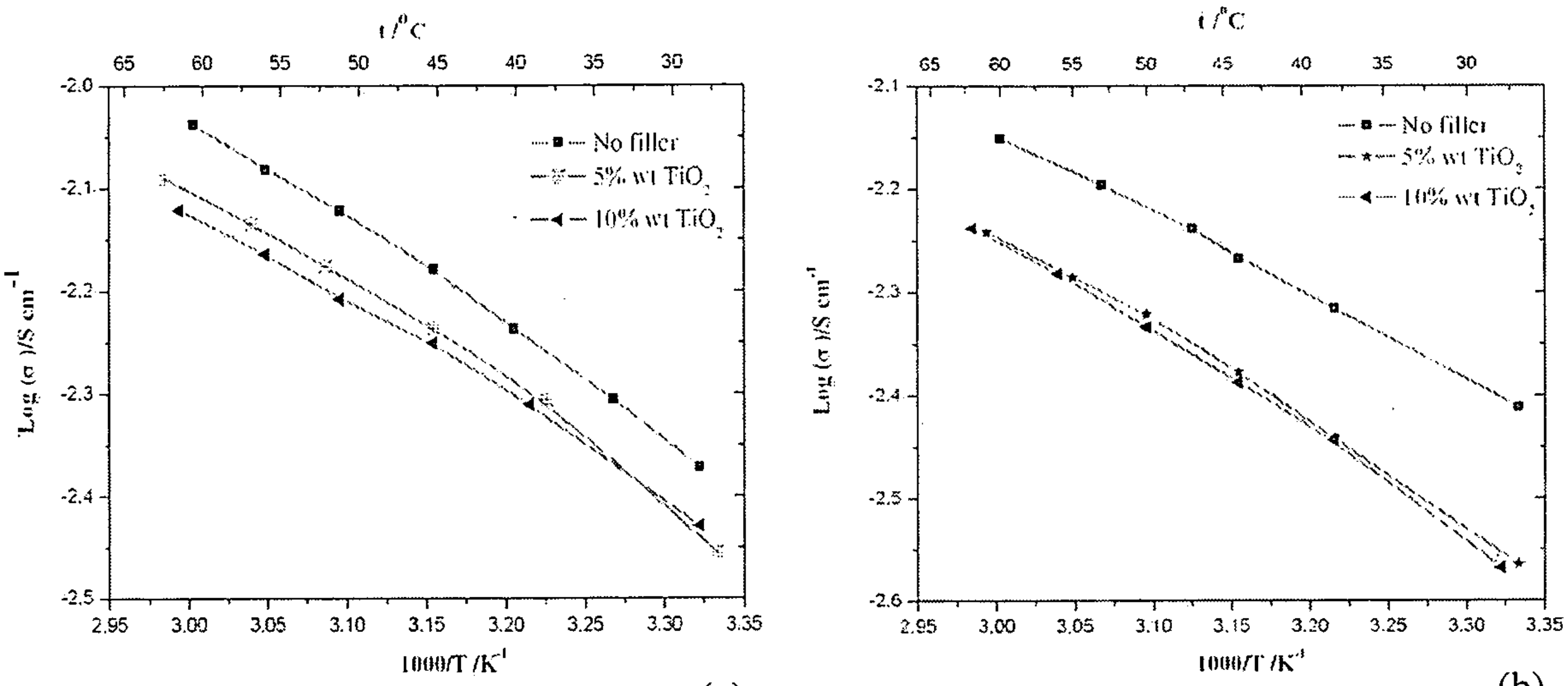


Figure 15: The graph of log (σ) vs. 1000/T

A shown in the Figure 15 the highest conductivity was observed by composition ***a***, which has the highest salt amount. But composition b was mechanically stable than composition *a*.However to identify the maximum conductivity composition the amount of EC and PC were reduced, in order to increase the amount of the salt.



(a) (b)

Figure 16: Temperature dependence of the ionic conductivity with the addition of the filler to (a) composition ***a*** (b) composition ***b***

As shown in the Figure 16(a) and Figure 16(b) the ionic conductivity of the both compositions do not show an enhancement after the addition of the filler. Among the polymer hosts studied, so far, the PAN based electrolytes offer a homogenous, hybrid electrolyte films in which the salt and the plasticizer were molecularly dispersed. Unlike in PEO the PAN host is inactive in the ionic transport mechanism but acts as a matrix for structural stability. So there is no segmental motion of the polymer chains as in the PEO polymer matrix. Hence the role of the filler in the PAN system is not significantly effect the ionic conductivity of the PAN-$LiBF_4$ system. But the filler addition has given a mechanical stability to the PE film (composition***a***) without a significant reduction of the ionic conductivity.

DC polarizing data

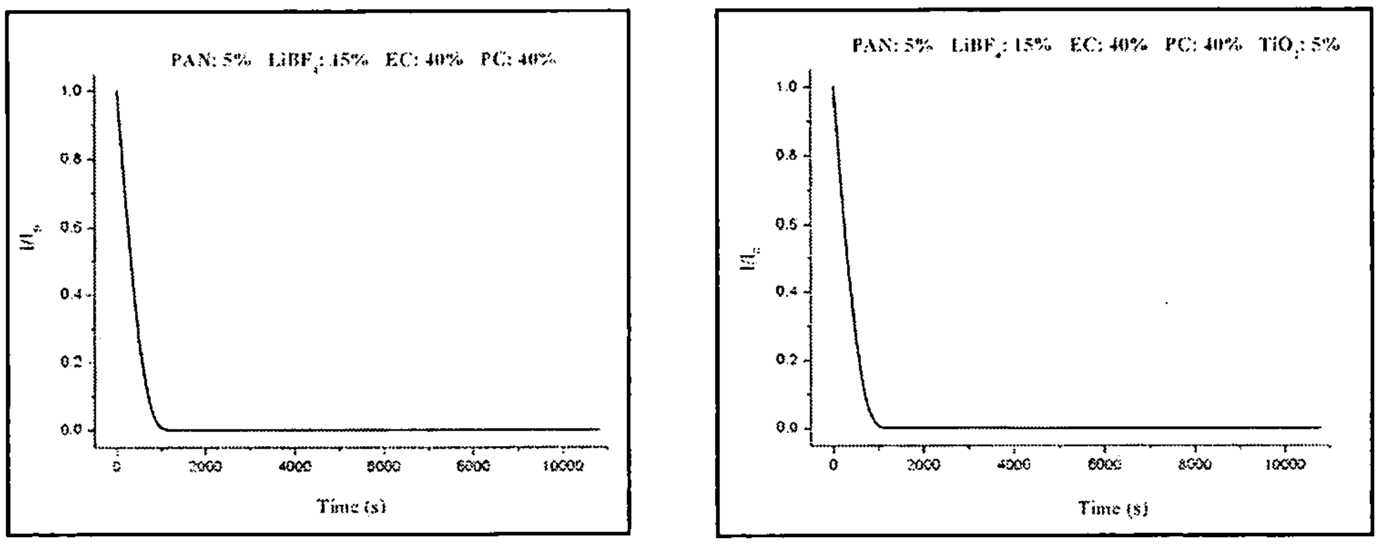


Figure 17: The graph of I/I_0vs time for filler free and filler added PEs.

The DC current showed an abrupt drop within first 10 mins for both filler free and filler added samples. So that it is concluded that the filler free and filler added gel polymer electrolyte samples are predominantly ionic conductors and the electronic conductivity is negligibly small.

Fourier transform infrared (FT-IR) spectroscopy

In order to determine the existence of interaction of $LiBF_4$ with plasticizers and the polymer used, IR spectra of a series of samples were obtained and the data was analyzed. The compositions of the electrolytes that were used for FT-IR studies are given below.

Table 04: Compositions of the electrolytes prepared for FT-IR studies

Composition	EC (g)	PC (g)	PAN (g)	$LiBF_4$ (g)
A	0.40	0.40	0.05	0.15
B	0.40	0.40	0.10	0.10
C	0.40	0.40	0.15	0.05
D	0.40	0.40	0.20	0.00

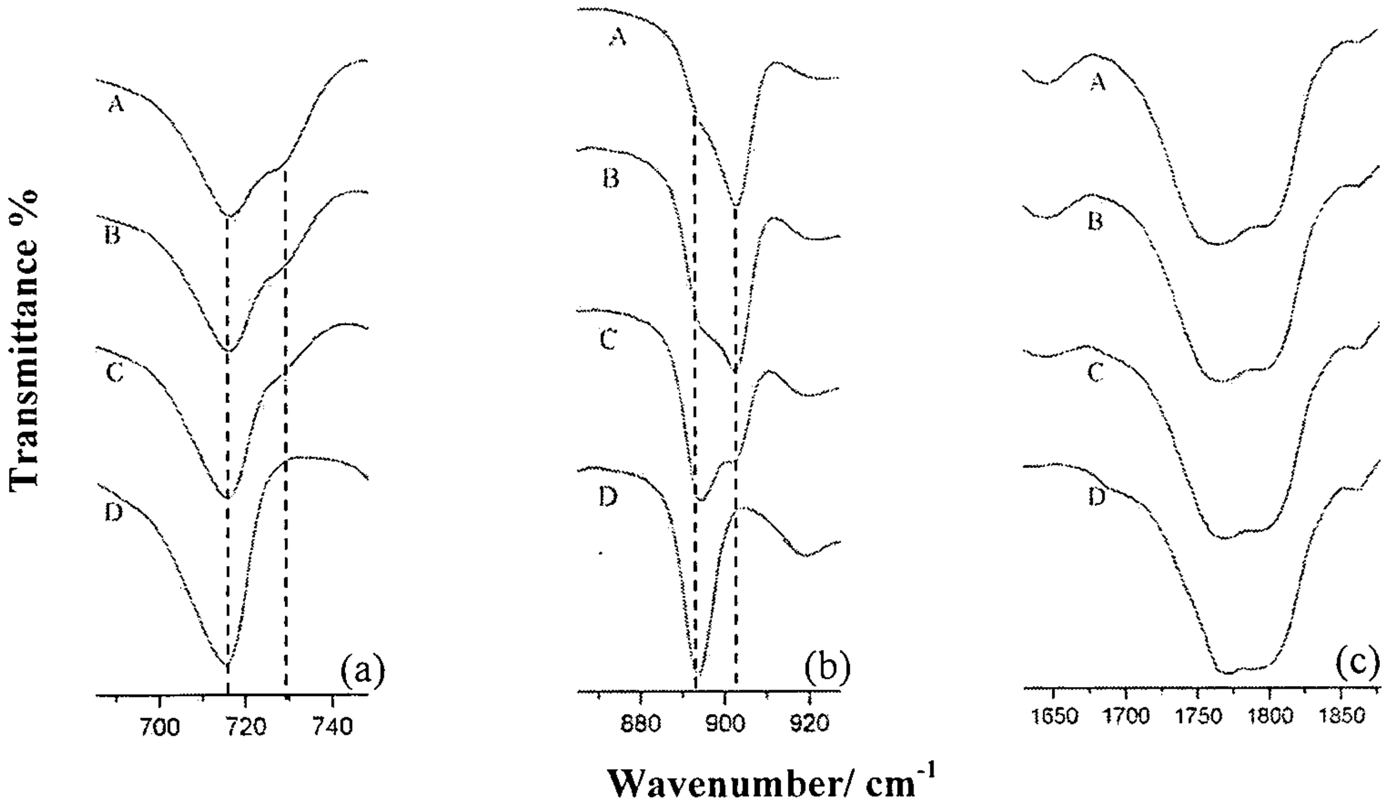


Figure 18: FT-IR spectral mode corresponds to (a) ring bending of EC and symmetric ring deformation of PC (b) ring breathing of EC (c) C=O symmetric stretching of EC and PC

Figure 18 shows the FTIR spectra of PAN based polymer electrolytes with different concentrations of $LiBF_4$. Two remarkably changed bands were identified, which are located at 716 cm^{-1} and 893 cm^{-1}. It can be seen that the peak at the ~ 716 cm^{-1} for composition ***D*** became a doublet at 716 cm^{-1} and 729 cm^{-1} with the increase of the $LiBF_4$ concentration. The peak appearing at 729 cm^{-1} is corresponding to ring bending and ring deformation modes of EC and PC molecules bonded to Li ions. The shifts of vibrational frequencies are consistent with the observations of Zhaoxiang Wang *et. al.* (Wang *et. al.*, 1996) in a study of EC interactions with $LiClO_4$ and Battisti*et. al.* (Battisti*et. al.*, 1993) in a study of PC interactions with $LiClO_4$.

Using Origin-Pro 8 software, a band fitting was done for the spectral range 680 cm^{-1} to 740 cm^{-1}. For composition***D*** the strong contour is separated into two components at 712 and 716 cm^{-1}. These components were identified as the ring bending mode of EC (716 cm^{-1}) and symmetric ring deformation of PC (712 cm^{-1}). As the salt concentration increases another component is appearing at around 729 cm^{-1}, corresponding to the interaction between Li^{+} and plasticizers (Shawna *et. al.,* 1997; Zhaoxiang*et. al.,* 1996; Battisti*et. al.,* 1993)

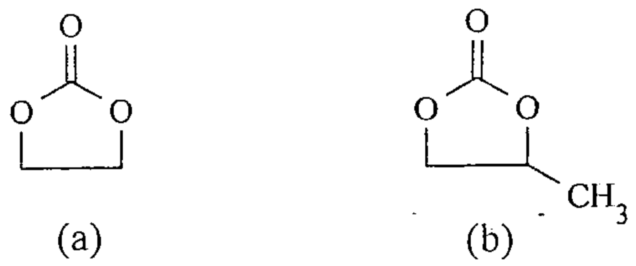
The area of the peak at 712 cm^{-1} which corresponds to the symmetric ring deformation of PC does not vary much with the addition of the salt. But the area of the peak at 716 cm^{-1} which corresponds to the ring bending of EC is decreasing while the area of the peak at 729 cm^{-1} is increasing with the addition of the salt. This concludes Li is more prominent to interact with oxygen in the ring group of EC.

Table 05: Percentages of areas of each component peaks in the spectral range 680 cm^{-1} to 740 cm^{-1}

			729 cm^{-1}			
	712 cm^{-1}	**716 cm^{-1}**	Area obtained from band fitting	Area calculated from 903 cm^{-1} peak	**893 cm^{-1}**	**903 cm^{-1}**
A	61 %	21 %	18 %	18.1 % (67%/3.7)	33 %	67 %
B	60 %	29 %	11%	11.1 % (41%/3.7)	59%	41 %
C	57 %	34 %	9 %	8.6 % (32%/3.7)	68%	32 %
D	62 %	38 %	-	-	100%	-

Similar band splitting phenomena was also observed in the mode corresponding to the ring breathing mode of EC (Figure18(b)). Here, the mother peak at 893 cm^{-1} was split into 893 cm^{-1} and 903 cm^{-1} with the increase of salt concentration. With the addition of 15% LiBF$_4$ to the composition ***C***, a strong peak was observed around 903 cm^{-1} with a weak shoulder around 893 cm^{-1}. Peak fitted data is summarized in the Table 05. The percentage of peak area of the band at 903 cm^{-1} increase with the salt concentration and the percent area of the peak at 729 cm^{-1} is a factor of the percent area of the band at 903 cm^{-1} as given in the Table 05. This reveals that Li^{+} is predominantly interacting with EC.

According to literature (Biying*et. al.,* 1996) EC has a pair of intense doublets at ~1770 cm^{-1} and 1798 cm^{-1} corresponding to C=O symmetric stretching mode. The position of these two peaks does not vary with the addition of PAN/ LiBF$_4$, but the peaks broadening can be observed. The band splitting towards the higher frequency level observed here should be accommodated strong interaction between the Li^+ ion of $LiBF_4$ and the oxygen atoms of the ring group (Figure 19) of plasticizers EC and PC (including both the C=O and C-O bonds).



(a) (b)

Figure 19: Chemical structure of (a) EC and (b) PC

Battery characterization

The cells were subjected to 5 mA charge-discharge current at room temperature using the Maccor Battery tester. The upper voltage limit was 4.2 V and the lower voltage limit was 0.5 V. the open circuit voltage was about 1.5 V.

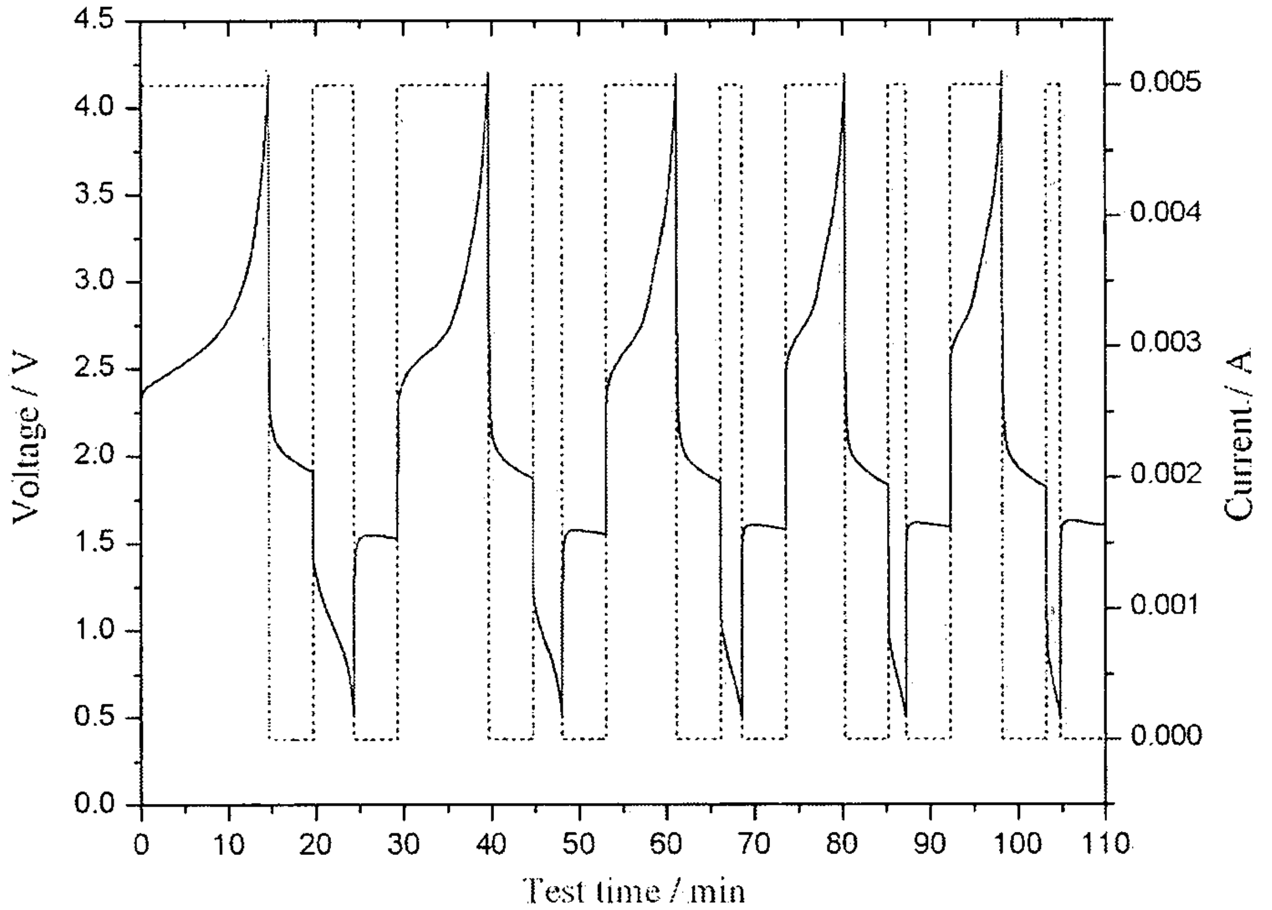


Figure 20: Charging discharging profiles of cell fabricated using GPE with composition *b*(with 10% wt TiO_2)

System 4.Tetraglyme/KI/Fumed silica based gel polymer electrolyte system

DC Polarizing Technique

The Wagner's DC polarization test was performed for both liquid and gel polymer electrolytes. This method was used to analyze the mobile species in the electrolyte. The DC current variation as a function of time of GPE with 10%wt fumed silica and at a O:I ratio 15:1 is shown in Figure 21.The DC current showed an abrupt drop within first 10 minutes for both liquid and gel samples due to the blocking effect of the electrodes. Charge carriers of the form of ions are blocked at the electrode-electrolyte interface and after some time the current become constant which is corresponded to the current due to electrons. According to our data it is concluded that the both liquid and gel polymer electrolyte samples investigated are predominantly ionic conductors with negligible electronic conductivity.

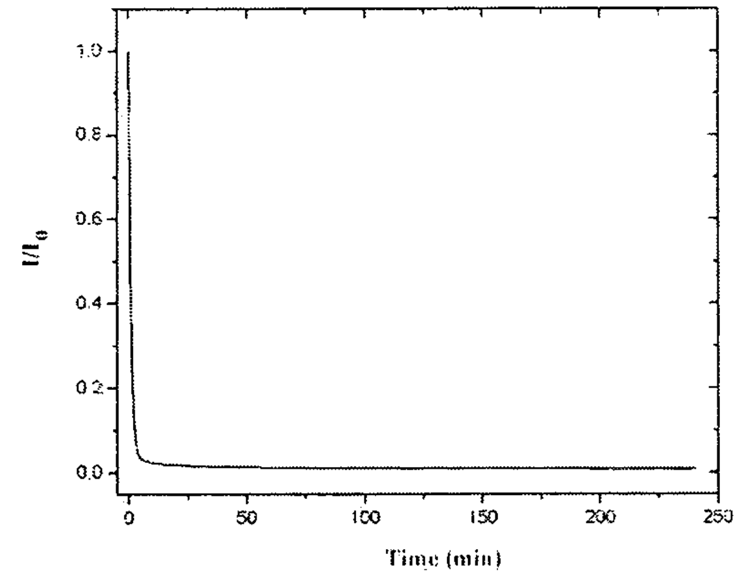
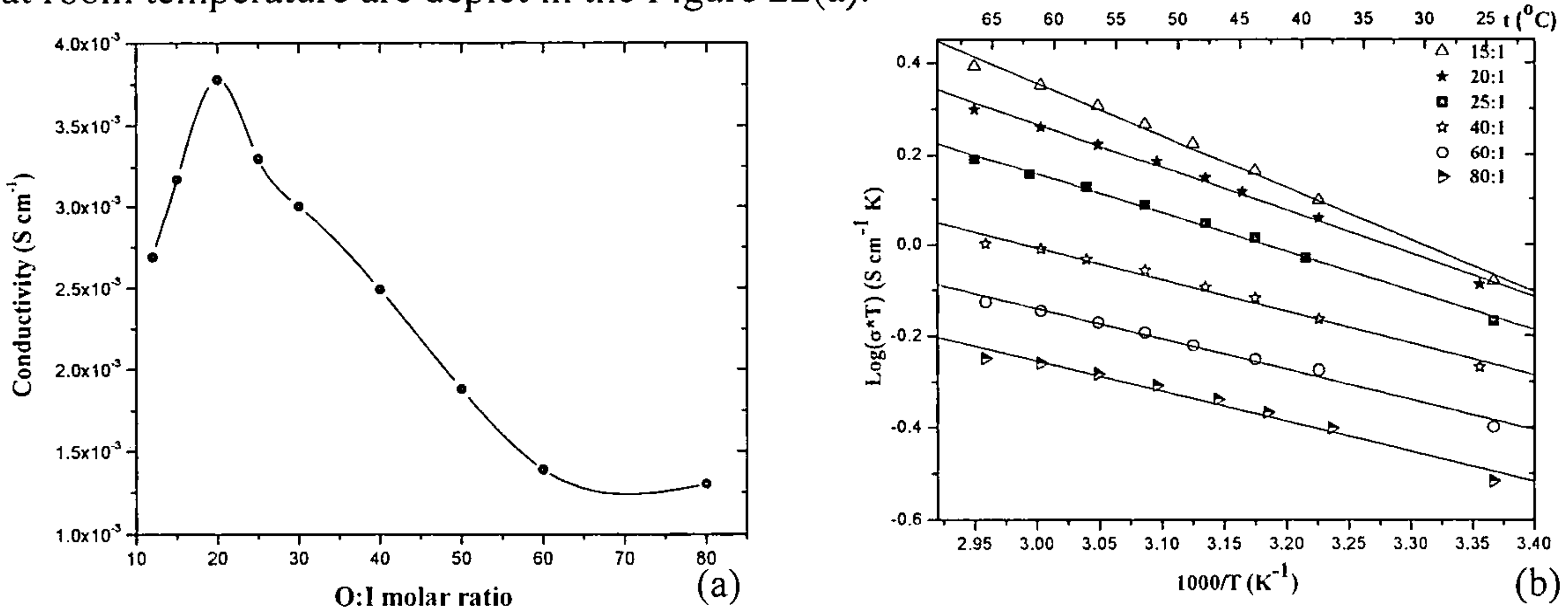


Figure 21: The DC current variation as a function of time of GPE with 10%wt fumed silica and at a O:I ratio 15:1

Complex Impedance Measurements

The ionic conductivities of the (tetraglyme)$_n$KIliquid electrolytes with different O:I molar ratios at room temperature are depict in the Figure 22(a).



(a)

(b)

Figure 22: (a) The ionic conductivities of the liquid electrolytes with different O:I molar ratios (b) The ionic conductivities of the GPEs with 10% wt SiO_2 with different O:I molar ratios.

The highest ionic conductivity of 3.78×10^{-3} S cm^{-1} was obtained at room temperature for the electrolyte sample with O:I molar ratio of 20:1.

Preheated fumed silica was added as 10% wt. of the total weight of tetraglyme and KI to the liquid electrolytes with molar ratios 80:1, 60:1, 40:1, 20:1, and 15:1 to form a GPE. The temperature dependence of the ionic conductivities of prepared GPE samples are shown in Figure 22(b).

The conductivity variation of all GPEs well obeys Arrhenius relationship: within the tested temperature range, where E_a is the activation energy, σ_0 is the pre-exponential factor, k is the Boltzmann constant and T is the absolute temperature.

$$\sigma T = \sigma_0 \exp\left[\frac{-E_a}{kT}\right]$$

After addition of the fumed silica GPE with 15:1 molar ratio exhibit the highest ionic conductivity of 2.80×10^{-3} S cm^{-1} at room temperature. However, compare to the liquid electrolyte system, after formation of the gel, samples with the similar concentrations were observed with lower ionic conductivity at room temperature. This may occur due to the hindrance cause by the silica to the motion of polymer chains. GPE with molar ratio 20:1 shows a low ionic conductivity than 15:1, while it gives the highest ionic conductivity in the form of liquid electrolyte. The high ionic conductivity of 15:1 GPE may be due to its high KI concentration, so that the reduction in the ionic conductivity cause by the addition of fumed silica is relatively low compared to the 20:1 GPE sample.

Furthermore 8% wt of fumed silica was added to the liquid electrolytes with 15:1 molar ratio. Figure 23 shows the comparison of the conductivity profile of GPEs with 10% wt silica and 8% wt silica at O:I ratio of 15:1.

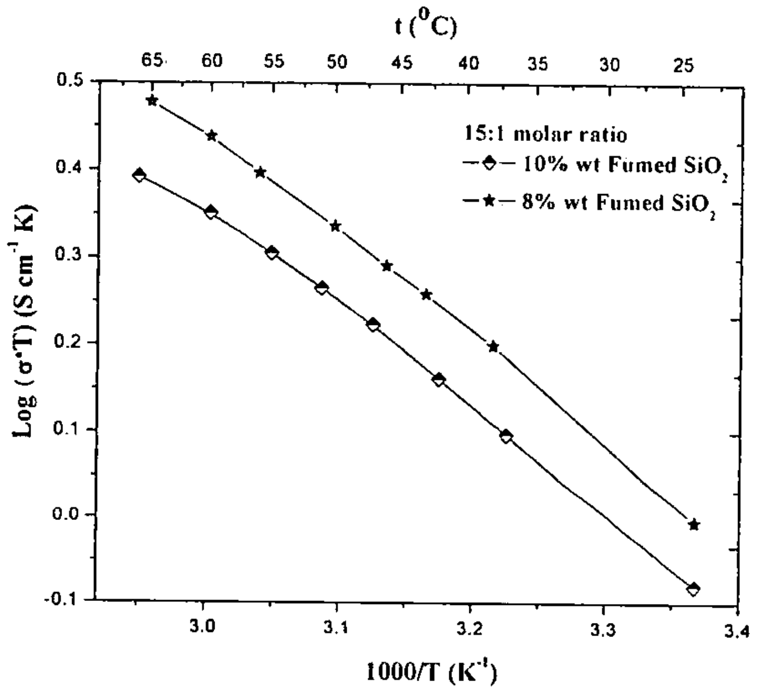


Figure 23: The ionic conductivities of the GPEs with 10% wt SiO_2 and 8% wt SiO_2, at a O:I molar ratio of 15:1.

When the amount of the fumed silica increased the conductivity tends to decrease as the silica rigid the electrolyte to form a gel. In this system fumed silica with surface silanol groups (Si-

OH) are behaved as the gelation agent. The main driving force to form a gel is believed to be the hydrogen bond between silanol groups on adjacent silica molecules or hydrogen bonds between silanol groups of silica molecules and ether oxygen of tetraglyme molecules.

FT-IR Measurements

In the present study the FT-IR vibrational spectroscopy has been used to study the interactions between the cation and the polymer. In the FT-IR spectra, bands between 800 cm^{-1} and 950 cm^{-1} have been assigned to modes of CH_2 wagging and C-O-C stretching motions. As depicted in the Figure 24(A), FT-IR spectrum of pure tetraglyme shows a band centered at850 cm^{-1} and with the increasing salt concentration a weak shoulder is appearing at ~862 cm^{-1}. This weak shoulder is due to the CH_2 wagging and CH_2 twisting motions of C-O-C-C-O-C units which interacts with the K^+ ions.

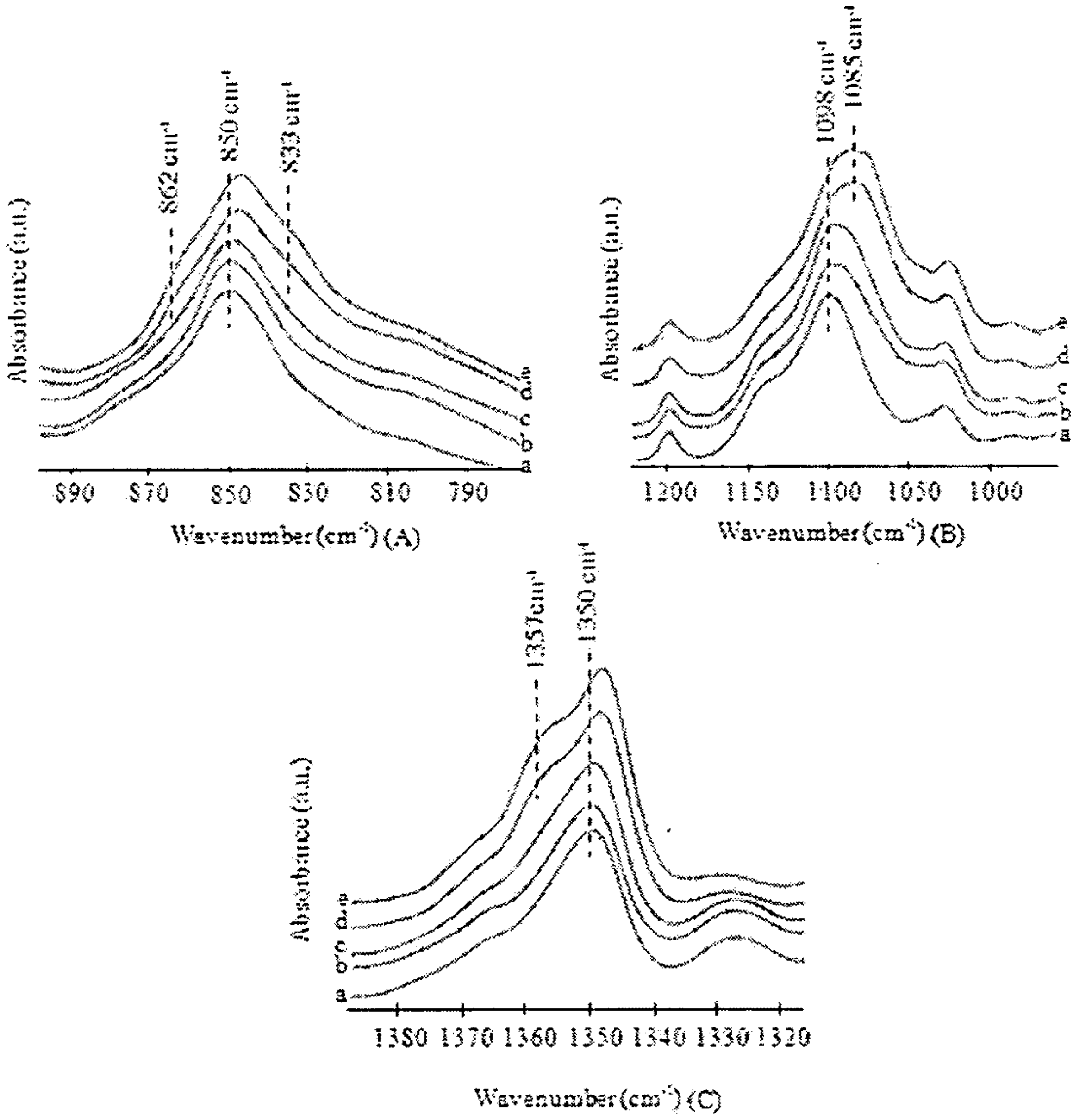


Figure 24: FT-IR spectra of a-liquid tetraglyme, b-gel tetraglyme (tetraglyme+ fumed SiO_2), c-(Tetraglyme)$_{80}$KI GE, d- (Tetraglyme)$_{20}$KI GE and e- (Tetraglyme)$_{15}$KI GE at room temperature in the (A) 780 cm^{-1} – 890 cm^{-1} spectral region (B) 950 cm^{-1} – 1220 cm^{-1} spectral region (C) 1320 cm^{-1} – 1390 cm^{-1} spectral region.

As shown in the Figure 24(B), the band appearing at the 1098 cm^{-1} of pure tetraglyme has been assigned to modes of CH_2 wagging. With the addition of the KI salt this peak showing a downshift to 1085 cm^{-1} for liquid electrolyte with 12:1 molar ratio which indicates the K^+ interactions with ether oxygen of the tetraglyme.

FT-IR spectra of pure tetraglyme and (tetraglyme)$_n$KI liquid electrolytes with different O:I molar ratios at room temperature in the 1310 cm^{-1} – 1410 cm^{-1} spectral region is shown in Figure24(C). As seen in the spectrum of pure tetraglyme and (tetraglyme)$_n$KIliquid electrolytes, a weak shoulder is appearing in the range 1310 cm^{-1} – 1410 cm^{-1}spectral region. The band appearing at 1350 cm^{-1} in tetraglyme has been assigned for CH_2 rocking. With the addition of the salt to the tetraglyme the band was split further to give an additional component at ~1359 cm^{-1}.

Solar cell fabrication and characterization

The gel polymer electrolyte based Dye sensitized solar cells (DSSC) were fabricated by sandwiching the electrolyte film in between Platinum (Pt) coated FTO electrode and dye absorbed TiO_2 electrode with configuration Glass / FTO / TiO_2 / Dye / solid electrolyte /Pt / FTO / Glass . The photocurrent–voltage (I–V) characteristics of the cells were measured under the illumination of Portable solar simulator Peccell (PEC-L01) using a computer controlled setup coupled to a Keithley 2400 Source meter.

Table 06: Solar cells parameters of the DSSCs for 20:1 liquid electrolytewith and without fumed silica.

Polymer Electrolyte	**J_{sc} (mA cm^{-2})**	**I_{sc} (mA)**	**Efficiency (%)**	**Fill Factor (%)**	**V_{oc} (mV)**
$(G4)_{20}$KI+ 10% wt SiO_2	13.40	3.35	4.76	52.24	680
$(PEO)_{20}$KI	14.48	3.62	4.97	52.78	650

vi. Conclusions

In the first system, we found that the addition of TiO_2 has not increased the I^- conductivity significantly, although the amorphous nature of PEO-$Pr_4N^+I^-$ samples has increased. Also the poor conductivity of the above system and the low efficiencies of the DSSCs fabricated show that the solid PEO-$Pr_4N^+I^-$ is not a good candidate for DSSCs.

Since PEO did not show strong interactions with bulk cation Pr_4N^+, LiTf was incorporated with PEO and characterized under various techniques to further study the effect of TiO_2 and raw illmenite. DC polarizing test confirmed the ionic nature of the prepared filler free and filler added SPEs. The highest conductivity within the studied temperature range was exhibited by the SPE with O:Li molar ratio10:1. However to investigate the filler effect, 20:1 composition was chosen due to it's relatively high ionic conductivity and less amorphous nature compared to the 10:1 composition. The ionic conductivity has been further enhanced by addition of the fillers TiO_2 and Ilmenite. The highest conductivity has been showed with the addition of 10% wt of the filler TiO_2 and 15% wtIlmenite. A reduction in the spherulite size in the optical micrographs of filler added SPE films was observed. This confirmed the enhancement of the ionic conductivity with the addition of fillers, as it affect reduction of the amorphous nature of the SPEs. XRD spectra were also suggested that the amorphous nature of the SPEs has increased after addition of Ilmenite.

In the PAN/$LiBF_4$/EC/PC gel polymer electrolyte system, the maximum conductivity 4.25×10^{-3} S cm^{-1} was observed for the GPE sample contains highest salt concentration (composition ***a***). However its mechanical stability was poor compared to the composition ***b***. The filler (TiO_2) was improved the mechanical properties of the GPEs without significant reduction of the ionic conductivity. The prepared GPEs with and without filler were predominantly ionic conductors with negligibly small electronic conductivity. According to the FT-IR spectra of GPEs, the changes in the band shape, band width and vibrational frequencies indicated that there is strong interactions of L^+ ions of dissociated $LiBF_4$ with the ring and C=O group of the plasticizer molecules.

Since the cation-plasticizer interaction is found to be strong in the PAN/$LiBF_4$/EC/PC gel polymer electrolyte system, a Solvent/Salt/Fumed silica based GPE system was studied. By mixing low molecular weight tetraglyme and KI based liquid electrolyte with fumed silica, a GPE, which possess good mechanical strength, was successfully fabricated. The prepared GPEs were predominantly ionic conductors. However the addition of fumed silica to liquid electrolyte forms a gel with a promising ionic conductivity. The highest ionic conductivity of 2.80×10^{-3} S cm^{-1} at room temperature was observed for the GPE sample with O:I molar ratio 15:1 incorporate with 10% wt fumed silica. According to the FT-IR spectra of liquid electrolytes, the changes in the band shape and vibrational frequencies indicated that there is a strong interaction of K^+ ions of dissociated KI with the ether oxygen of tetraglyme chains.

vii. References

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viii) Problems if any, encountered during the implementation of the project

There were two issues related to project implementation. After the procurement process, the time taken to deliver chemicals was about three to four months, at certain times the chemicals were never delivered. This was very inconvenient for the smooth functioning of the project. Also the prizes of the major equipment that we were anticipating buying had increased, by the time the grant was received and quotations were called.

ix) Major findings and follow up activities

The addition of an inert ceramic filler does not enhance the ionic conductivity in large cation systems, when only the anion conductivity is predominant.

Commercial TiO_2 and raw illmenite show similar effects as ceramic fillers in solid polymer electrolytes with small cation salts. That is, the amorphous nature is reduced and the ionic conductivity is increased.

Small cations have strong interactions with the solvents such as EC and PC, and the gel electrolytes show promising conductivities as electrolytes with better mechanical properties compared to liquid electrolytes.

A liquid electrolyte based on tetraglyme and KI was turned to a gel electrolyte using fumed silica and showed that close efficiencies can be obtained using the liquid and the gel electrolytes.

As a follow up activity, we suggest that more gel electrolytes prepared using fumed silica and various solvent-salt systems to be synthesized and characterized, as these gel electrolytes show promising results.

Section 4

Relevance of results achieved to scientific advancement

Our results show the absence of large cation-polymer interactions and that there is no enhancement of anion conductivity due to addition of nano fillers. Addition of nano fillers is widely used to improve the conductivity, but our study show that fillers do not improve the anion conductivity although the amorphous nature of the samples is increased.

The study on new lithium and PAN based gel polymer electrolyte contributes to the existing knowledge on polymer gel electrolytes. Especially the findings related to cation-plastisizer interaction paved the way to synthesis a new polymer free gel electrolyte.

A new polymer free gel electrolyte was synthesized with promising ionic conductivities. A systematic study had been carried out to characterize the prepared gel electrolytes. A thorough study to understand the stability and mechanism of gel formation is recommended which will lead towards making commercial products.

Relevance of results achieved to national/socio economic development

Currently the rutile and illemenite from ores in Sri Lanka are exported as raw materials without any value addition. If these natural minerals can be used after an R and D phase as a component in rechargeable batteries, their commercial value can be enhanced.

Some of the research findings from this research project may have the possibility, after going through a R&D phase, to initiate an industry for the manufacture of rechargeable batteries in Sri Lanka. This can indirectly contribute towards the economic development in the country and to alleviate poverty of people. The new electrolyte materials developed under this project are environmentally friendly and these materials, as well as the devices made from the materials will have no adverse effect on the environment.

We have provided comprehensive research training to a Postgraduate student at M.Phil. level through this project, thus contributing to human resource development in R&D in the area of technologically important novel materials. The student will be completing the M.Phil. degree within a year.

iii) Dissemination/application of research output

Several presentations related to project work have done in international and local conferences. Two manuscripts are being prepared to be published in reputed journals. Certain systems studied under this project can be used in electrochemical devices after undergoing comprehensive research and development phase.

Section 5

Miscellaneous

i. List of major equipment acquired during the project period and their functionality
None: The cost of the equipment was higher than the awarded amount for the equipment vote. We did not anticipate such a prize change from the prize given during the proposal writing period.

ii. List of publications/ communications arising from the project and/or presentations made at seminars, workshops etc.

Conference Proceedings (Full papers):
Please find the copies in the Annexure I

1. K.V.L. Amarasinghe, V.A. Seneviratne, L.R.A.K. Bandara, M.A.K.L. Dissanayake, "Electrical and Optical Studies on PAN-$LiBF_4$ Based Gel Polymer Electrolytes", Proceedings of the Special Session on Advanced Materials, 4th International Conference on Structural Engineering and Construction Management (ICSECM), 2013, page 118-128.

2. K.V.L. Amarasinghe, V.A. Seneviratne, L.R.A.K. Bandara and M.A.K.L. Dissanayake, "Electrical And FT-IR Study of Fumed Silica Based Gel Electrolytes; $(Tetraglyme)_nKI$ And $(Ethylene\ Glycol)_nKI$", 14th Asian Conference on Solid State Ionics (ACSSI), 2014, page 512-521.

Abstracts:

4. K.V.L. Amarasinghe, V.A. Seneviratne, L.R.A.K. Bandara, A.K. Arof and M.A.K.L. Dissanayake, "An investigation of anionic conductivity of the Composite Polymer Electrolyte based on PEO and $Pr_4N^+I^-$ salt with the filler TiO_2", Procedings of the technical sessions, International Symposium on Polymer Science and Technology 2012 in Collaboration with Industries, Institutions and Universities (IIUPST), 2012, page 31.

5. K.V.L. Amarasinghe, V.A. Seneviratne, L.R.A.K. Bandara and M.A.K.L. Dissanayake, "Ionic Conductivity and FT-IR Study of Tetraglyme/KI/ Fumed Silica Gel Polymer Electrolyte", Peradeniya University International Research Session (iPURSE), 2014, page 465.

6. S.H.R.T. Sooriyagoda, K.V.L. Amarasinghe, B.S. Dassanayake, V.A. Seneviratne, "Effect of Ilmenite as a Filler in the Polymer Electrolyte $(PEO)_{20}LiTf$", Peradeniya University International Research Session (iPURSE), 2014, page 448.

Section 6

	Funds allocated / Rs.	Funds received / Rs.	Total expenditure / Rs.	Balance available / Rs.
Personal	965 166	600 000	965 166	-365 166
Equipment	600 000	600 000	-	600 000
Consumables	500 000	500 000	225 552.26	*274 447.74
Travel & subsistence	80 000	40 000	14 034.68	25 965.32
PG registration fee	40 000	20 000	44 500	-24 500
Miscellaneous	40 000	25 000	6 014	18 986
Total	**2 070 000**	**1 785 000**	**1 252 266.94**	**532 733.06**

Funds received	1 785 000.00
Actual expenditure	1 252 266.94
Balance	**532 733.06**
***Commitments**	**Rs 281 562.40**

Section 7

i) Grantee's signature:

Dr. V.A. Seneviratne:

Dr. L.R.A.K. Bandara

ii) Comments of the Head of the Department/Signature

— Successfully Completed —

Dr. L. R.A.K. Bandara
Head
Department of Physics
University of Peradeniya
Peradeniya, Sri Lanka.

iii) Head of the institution's signature

Prof. H M D Namal Priyantha
Director
Postgraduate Institute of Science
University of Peradeniya
Sri Lanka.

Annexure

IUPST
SYMPOSIUM 2012

Providing innovative solutions
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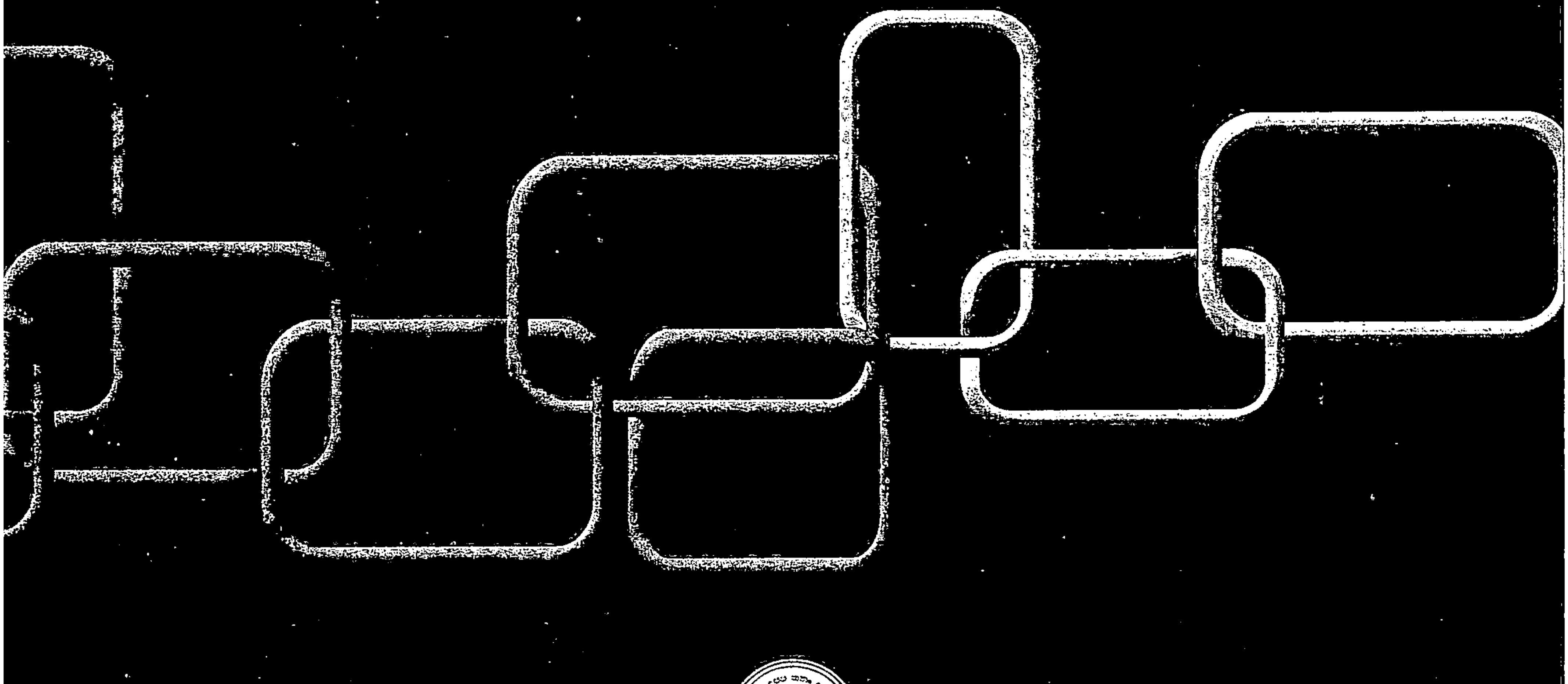
International Symposium on Polymer Science and Technology 2012 in Collaboration with Industries, Institutions and Universities



Organized by:

Department of Chemistry, University of Sri Jayewardenepura

An investigation of anionic conductivity of the composite polymer electrolyte based on PEO and $Pr_4N^+I^-$ salt with the filler TiO_2

K. V. L. Amarasinghe,[1] V. A. Seneviratne,[2]* L. R. A. K. Bandara,[2] A. K. Arof,[3]
and M. A. K. L. Dissanayake [2,4]

Polymer Electrolytes (PEs) have been studied to use in many devices such as lithium rechargeable batteries, fuel cells, electrochromic devices, etc. Most of the previous research work has been carried out to study the cation conductivity of PEs and their conductivity enhancement with the addition of various fillers. There are not many reports on studying the effect of filler on anionic conductivity in PEs. In this study, the anion conductivity was investigated using the anion conducting PE with tetrapropylammonium iodide ($Pr_4N^+I^-$) as the salt, polyethylene oxide (PEO) as the polymer and titanium dioxide (TiO_2) as the filler.

The solvent casting method was used to prepare PE samples, $(PEO)_mPr_4N^+I^-$ (m = 5, 10, 20, 30, 40, 50, 60, 80 and 90), where m:1 is the O:I (oxygen:iodine) ratio of the samples. The solvent casting method yielded visually homogeneous composite PE films with average thickness of 100 – 400 μm. Estimated conductivities of the filler free samples were in the order of 10^{-9} S cm^{-1} at room temperature and relatively high anionic conductivity was observed for the samples $(PEO)_{60}Pr_4N^+I^-$ and $(PEO)_{50}Pr_4N^+I^-$. The filler was added as a weight percent (5%, 10%, 15%, 20% and 30%) to the 60:1 and 50:1 samples. The thermal studies were carried out to investigate the melting enthalpies of the filler free and filler added samples using the Pyris 1 differential scanning calorimeter (DSC).

Unlike the cation conducting PEs, here the anionic conductivity did not increase with the addition of the filler. However according to the conductivity and DSC results it can be concluded that the amorphous nature of the samples was increased. Optical micrographs confirmed this nature showing a reduction in size of the spherulites with addition of the filler.

Keywords: Anionic conductivity / Tetrapropylammonium iodide / Polymer electrolyte / Filler effect / Polyethylene oxide

Acknowledgement: National Science Foundation and National Research Council of Sri Lanka.

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4th International Conference on

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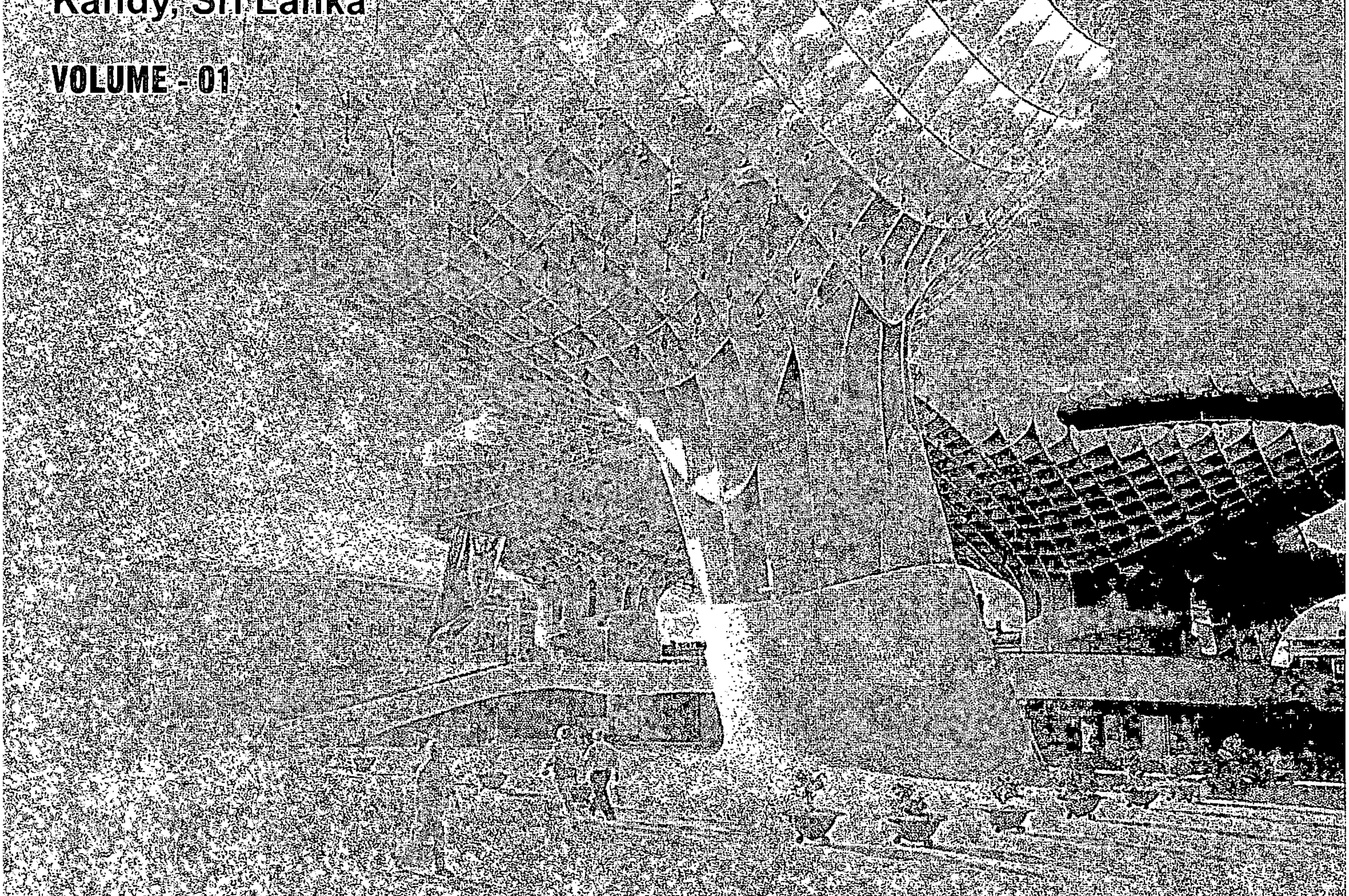

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ELECTRICAL AND OPTICAL STUDIES ON PAN-$LiBF_4$ BASED GEL POLYMER ELECTROLYTES

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Abstract:

Gel Polymer Electrolytes (GPEs) are promising materials for the ever-growing need of high energy density power sources such as lithium ion batteries. The emphasis of this work is on a plasticized polyacrylonitrile (PAN) and lithium tetrafluoroborate ($LiBF_4$) based GPE system with and without ceramic filler titania (TiO_2). As the plasticizer, a mixture of ethylene carbonate (EC) and propylene carbonate (PC) at a ratio 1:1 was used. All GPE samples were prepared by selecting a fixed amount (80 wt %) of plasticizer with different weight percentages of the salt and the polymer. The ionic conductivities of all samples with different polymer to salt ratio are in the order of 10^{-3} S cm^{-1} at room temperature. FT-IR studies were carried out to investigate the interactions of Li^+ ions with PAN and plasticizers. Many vibrational frequency modes have been identified to verify the interactions of Li^+ ions with the plasticizers (EC and PC), which are mainly occurring with the oxygen atoms of the ring group of plasticizers (including both C-O and C=O bonds). The filler addition has given a mechanical stability to the GPEs without a significant reduction of the ionic conductivity. The high ionic conductivities suggest that these are good candidates as electrolytes for lithium ion battery applications.

Keywords: *Polyacrylonitrile, Gel polymer electrolytes, Filler effect, Plasticizers, FT-IR spectroscopy*

1.0 Introduction

The ever increasing demand for the energy production, storage and distribution has become the major goal and the challenge in the scientific world today. Among the various classes of solid state electrolytes such ascrystalline and composite electrolytes, solid polymer electrolytes (SPEs) and ionically conducting glasses, SPEs are identified as rather promising materials, especially due to their low weight, mechanical flexibility, possibility to obtain as thin films and low cost (Gray, 1991). These can be used in rechargeable batteries, fuel cells, solar cells, super capacitors, electrochromic devices etc after improving their conductivity and other parameters (Ileperuma *et al.*, 2004; Abraham *et al.*, 2006). The ionic conductivity in high molecular weight poly (ethylene oxide) (PEO) doped with sodium and potassium salts was first reported by Wright (1975) and the technological implications of these electrolytes were suggested by Armond *et al.* (Armond *et al.*, 1979). However, PEO-based SPEs offer very low ionic conductivity (~ 10^{-7} S cm^{-1}) values around ambient and sub ambient temperatures. The low ionic conductivity is due to the existence of crystalline polymer phase in SPEs. It is reported that in PEO based SPE systems, ion transport is highly taken place in the amorphous phase in which the ionic conductivity is greater as compared to the crystalline phase (Stainer *et. al*,. 1984).In order to obtain high ionic conductivity, SPEs should be more amorphous. Incorporating ceramic fillers or employing organic plasticizers or by using both these techniques, a selected SPE can be made more amorphous. The plasticizers enhance the ionic conductivity of SPEs due to many reasons such as weakening the interchain interaction, increasing free volume, decreasing of glass transition temperature (T_g) and creating ionically-conducting pathways in amorphous phase. On the other hand fillers enhance the ionic conductivity without degrading the mechanical and interfacial properties of SPEs (Dissanayake *et al.*, 2013).

Gel polymer electrolytes (GPEs) or plasticized polymer electrolytes, neither liquid nor solid or conversely both liquid and solid, are carrying both cohesive properties of solids and diffusive properties of liquids. In addition to this, solvent vaporization, electrochemical corrosion and leakage with the use of liquid electrolytes are greatly reduced with the use of GPEs.

The emphasis of this work is on a plasticized polyacrylonitrile (PAN) and lithium tetrafluoroborate ($LiBF_4$) based GPE system with and without ceramic filler titania (TiO_2). As a plasticizer a mixture of ethylene carbonate (EC) and propylene carbonate (PC) was used. Among the polymer hosts studied so far, polyacrylonitrile (PAN) based lithium salt complex has many advantages. It gives a high ionic conductivity and good mechanical stability at room temperature. The use of low molecular weight and high dielectric constant additives such as PC ($\varepsilon = 64.4$) and EC ($\varepsilon = 89.6$) impart salt solvating power and high ion mobility to the polymer electrolytes. It also increases amorphous content of the polymer matrix and tend to dissociate ion-pairs into free cations and anions thereby leading to an overall enhancement in conductivity.

2.0 Experimental details

Polyacrylonitrile (PAN) (average M_w 150 000), lithium tetrafluoroborate ($LiBF_4$) (98%), ethylene carbonate (EC) (98%), propylene carbonate (PC) and TiO_2 (particle size < 5μm, 99.9%) were purchased from Aldrich and used as starting materials. Prior to use EC, $LiBF_4$ and TiO_2 were vacuum dried at room temperature, 60 °C and 100 °C respectively. PC was used as received.

2.1 Preparation of GPE

In all the GPE samples prepared, the weight ratio of EC: PC was kept 1:1 and the weight of PAN and $LiBF_4$ were varied. The weighed amount of $LiBF_4$was dissolved in the EC/ PC mixture with the aid of magnetic stirring for half an hour until the salt is completely dissolved. Then PAN and the filler were added to the above solution and the mixture was heated at 140 °C while magnetically stirring for one hour. The resulting homogeneous viscous solution was casted on to a petry dish. After cooling, a transparent GPE could be obtained. The filler added GPE samples were prepared by adding TiO_2 as a percentage of the weight of polymer and salt.

Table 1: Compositions of the electrolytes prepared by varying PAN, $LiBF_4$, EC and PC

	Composition	EC (g)	PC (g)	PAN (g)	$LiBF_4$ (g)
System I	*a*	0.40	0.40	0.05	0.15
	b	0.40	0.40	0.10	0.10
	c	0.40	0.40	0.15	0.05
System II	*d*	0.35	0.35	0.05	0.25
	e	0.35	0.35	0.10	0.20
	f	0.35	0.35	0.15	0.15
	g	0.35	0.35	0.20	0.10

3.0 Sample characterization

3.1 Complex impedance measurements

After the formation of GPEs, disc shaped samples were sandwiched between two polished stainless steel blocking electrodes. The ionic conductivity of the samples was determined by the AC complex impedance technique with a computer controlled Solatron SI–1260 impedance analyzer in the frequency range of 20 Hz –10 MHz and in the temperature range of 27 °C to 60 °C.

The ionic conductivity (σ) of the electrolyte samples were calculated using the equation:

$$\sigma = \frac{l}{R_b A} \qquad (1)$$

where, R_b is the bulk resistance of the PE which was obtained from the graph of -Z″ (imaginary part) vs. Z′ (real part) of the electrical impedance, '*l*' is the thickness of the PE sample and '*A*' is the area of the sample.

3.2 Transference number measurement (DC polarizing technique)

In order to determine the ionic nature of the prepared electrolyte samples the DC polarizing test was carried out. In this technique a small DC voltage ~1 V was applied across a sample and the DC current through the sample was noted down as a function of time. Stainless steel (SS) electrodes were used as blocking electrodes in the SS/GPE/SS configuration; allow only free electrons if any to flow through an external circuit.

3.3 Fourier transform infrared (FTIR) spectroscopy

FTIR studies were performed in the attenuated reflection mode by using Thermo Nicolet 6700 FTIR spectrometer from 600 cm^{-1} to 4000 cm^{-1} in order to determine the existence of the interactions between Li$^+$ ion with plasticizers and the polymer used. The absolute resolution of the instrument is 4 cm^{-1}.

4.0 Results and discussion

4.1 Ionic conductivity

The possible mobile ion species of this electrolyte system are Li$^+$ and BF$_4^-$. The ionic conductivities obtained for all seven electrolyte samples at room temperature are listed in the Table 2.

Table 2: Ionic conductivity (σ) values obtained at room temperature for different compositions

	Composition	σ (10^{-3} × S cm^{-1})
System I	*a*	4.25
	b	3.88
	c	3.10
System II	*d*	2.32
	e	1.33
	f	0.98
	g	0.58

It can be seen from our data that the compositions, ***a***, ***b*** and ***c***, of system I, exhibit relatively high ionic conductivities compared to that of the four compositions of system II. Among the samples of system I, composition ***a*** shows the highest conductivity because of its high salt concentration. However, it shows a poor mechanical stability compared to sample *b* and *c* because of low PAN content. The ionic conductivity has increased with the salt concentration, due to the increase of mobile ion concentration in the polymer matrix.

The temperature dependence of the ionic conductivity of the above compositions is shown in the Figure 3. Within the studied temperature range, the shape of the curves is well fitted to the Arrhenius equation for gel electrolytes:

$$\sigma T = \sigma_0 \exp\left[\frac{-E_a}{kT}\right] \tag{2}$$

where, E_a is the activation energy, σ_0 is the pre-exponential factor, k is the Boltzmann constant and T is the absolute temperature.

The slope of the graph of log (σ) vs. 1000/T is a measure of the activation energy E_a of the PE sample. According to literature, at low and moderate salt concentrations, the activation energy is independent of the type of the salt used and it depends on the type of the plasticizer and the nature of the hetero-atoms or the functional group of the plasticizer (Matt *et. al*,. 2010; Matt *et. al.*, 2009). As observed in Figure 3, all slopes are not equal probably due to the high salt contents in the samples.

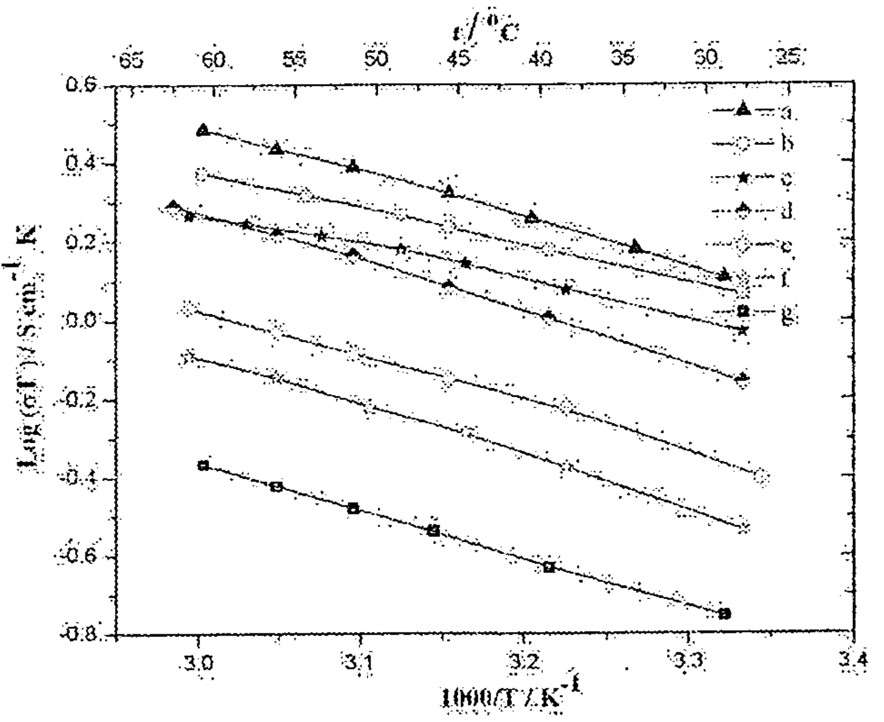
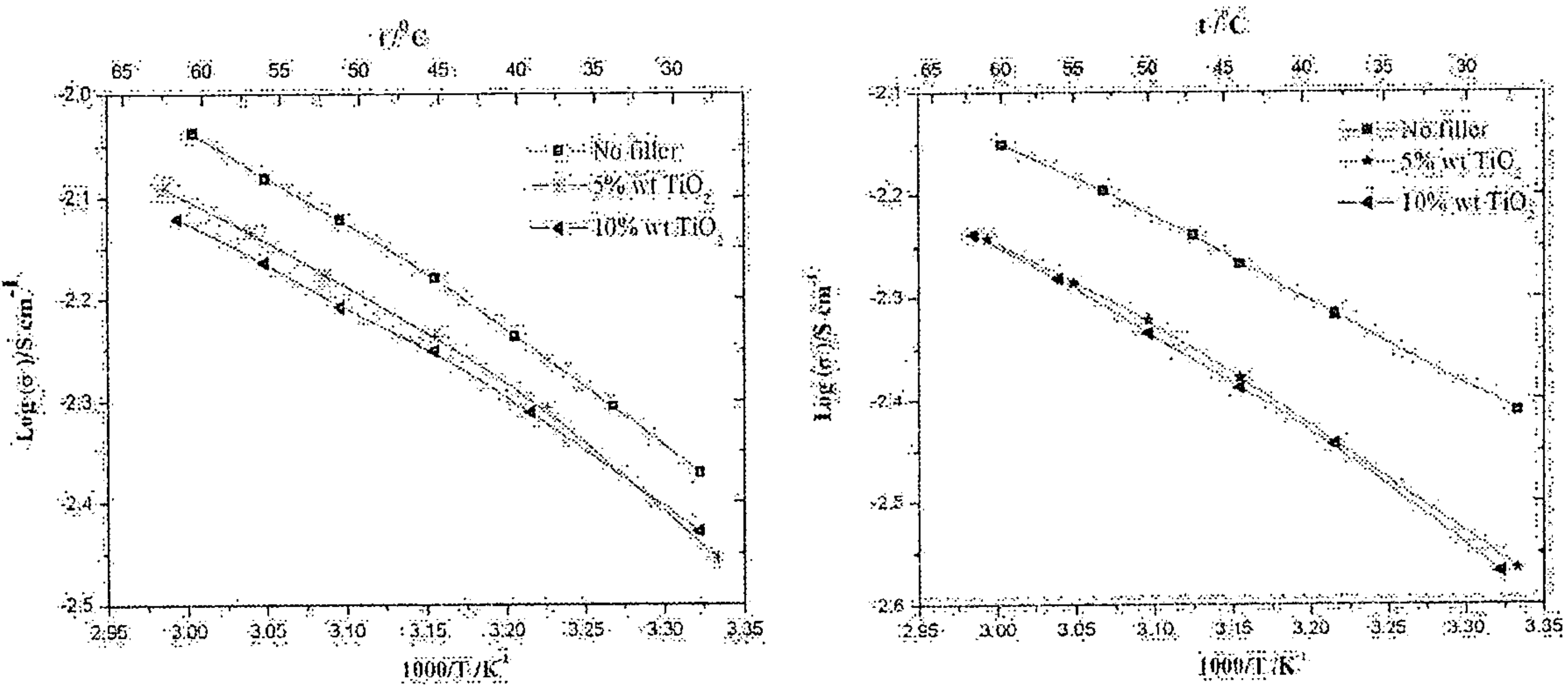


Figure 3: The graph of log (σ) vs. 1000/T

With reference to Table 1; salt concentration was increased by reducing the weight percentage of EC and PC from 80% to 70% (system II). The samples of system II have shown relatively low ionic conductivities than those of system I. Due to the reduction of EC and PC amount, the viscosity of the system was increased. This can be the reason for the observed low ionic conductivities of the samples in system II. Therefore, for further studies, only samples prepared under system I were considered.

The filler TiO_2 was added as a percentage of the total weight of PAN and $LiBF_4$ to the composition *a* as well as to composition *b*. Temperature dependence of the ionic conductivity of filler added samples are shown in Figure 4.



(a) Composition *a* **(b) Composition *b***

Figure 4: Temperature dependence of the ionic conductivity with the addition of the filler

As depicted in the above figure, the addition of the filler does not enhance the ionic conductivity but it has enhanced the mechanical strength of the PE samples. With addition of 5 wt% of TiO_2 to the composition *a*, the ionic conductivity achieved a value of 3.51 × 10^{-3} S cm^{-1} at room temperature and with addition of 10 wt% of TiO_2 the ionic conductivity was found to be 3.72 × 10^{-3} S cm^{-1} at the same temperature. With the addition of 5 wt% and 10 wt% of TiO_2 to the composition *b*, the ionic conductivity values were found to be around 2.72×10^{-3} S cm^{-1} for both samples at room temperature.

The addition of the plasticizers increases the free volume of the polymer matrix hence the mobile ions can move faster through the liquid-like phase. When ceramic filler like TiO_2 is added to this system, the filler particles also can be occupied in this free volume, which will be leading to a blocking effect. Due to this, the ion conduction through the polymer matrix can be disturbed and hence the reduction of the conductivity can be seen for the samples with moderate and high filler concentrations.

The ionic conductivity of all the PE samples studied in this research work increased with the increasing temperature. As the temperature increases, the polymer electrolyte can expand easily and the ions, solvated molecules, or the polymer segments are facilitated by the additional free volume created due to the increase of temperature. This enhances the ion and polymer segmental mobility that will, in turn, enhance the ionic conductivity.

4.2 DC polarization measurements

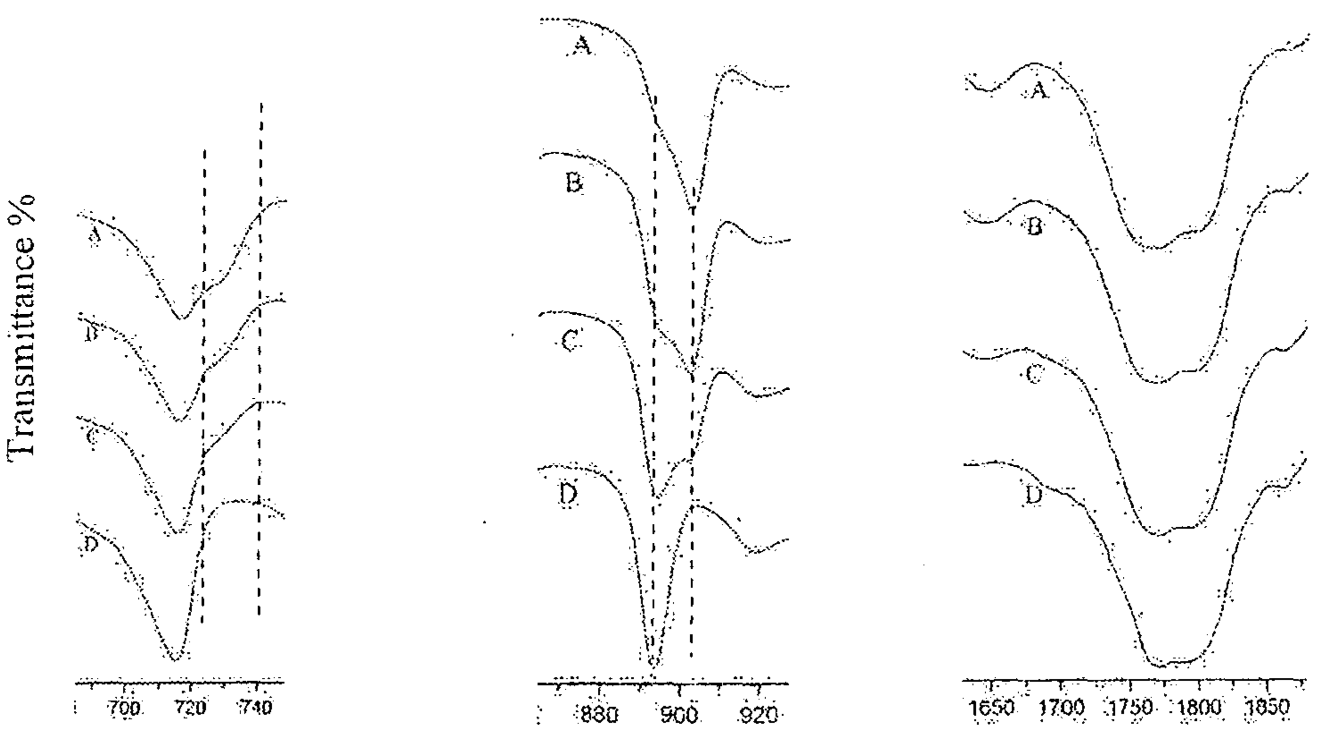
The DC polarization test was performed for both filler free and filler added samples. The ionic transference number of the mobile species in the polymer electrolyte was calculated by Wagner's dc polarization technique. This method was used to analyze the mobile species in the electrolyte. The DC current showed an abrupt drop within first 10 minutes for both filler free and filler added samples due to the ion migration at the electrode-electrolyte interface. After some time the current becomes a constant which corresponds to the current due to free electrons. According to our data it can be concluded that the filler free and filler added gel polymer electrolyte samples are predominantly ionic conductors with negligibly small electronic conductivity.

4.3 Fourier transform infrared (FT-IR) spectroscopy

In order to determine the existence of interaction of $LiBF_4$ with plasticizers and the polymer used, IR spectra of a series of samples were obtained and the data was analyzed. The compositions of the electrolytes that were used for FT-IR studies are given below.

Table 3: Compositions of the electrolytes prepared for FT-IR studies

Composition	EC (g)	PC (g)	PAN (g)	$LiBF_4$ (g)
A	0.40	0.40	0.05	0.15
B	0.40	0.40	0.10	0.10
C	0.40	0.40	0.15	0.05
D	0.40	0.40	0.20	0.00



(a) (b) (c)

Figure 5: FT-IR spectral mode corresponds to
(a) ring bending of EC and symmetric ring deformation of PC
(b) ring breathing of EC
(c) C=O symmetric stretching of EC and PC

Figure 5 shows the FTIR spectra of PAN based polymer electrolytes with different concentrations of $LiBF_4$. Two remarkably changed bands were identified, which are located at 716 cm^{-1} and 893 cm^{-1}. It can be seen that the peak at the ~ 716 cm^{-1} for composition ***D*** became a doublet at 716 cm^{-1} and 729 cm^{-1} with the increase of the $LiBF_4$ concentration. The peak appearing at 729 cm^{-1} is corresponding to ring bending and ring deformation modes of EC and PC molecules bonded to Li ions. The shifts of vibrational frequencies are consistent with the observations of Zhaoxiang Wang *et. al.* (Wang *et. al.*, 1996) in a study of EC interactions with $LiClO_4$ and Battisti *et. al.* (Battisti *et. al.*, 1993) in a study of PC interactions with $LiClO_4$.

Using Origin-Pro 8 software, a band fitting was done for the spectral range 680 cm^{-1} to 740 cm^{-1}. As depicted in the Figure 6, for composition ***D***, it can be clearly seen the strong contour is separated into two components at 712 and 716 cm^{-1}. These components were identified as the ring bending mode of EC (716 cm^{-1}) and symmetric ring deformation of PC (712 cm^{-1}). As the salt concentration increases another component is appearing at around 729 cm^{-1}, corresponding to the interaction between Li^+ and plasticizers (Shawna *et. al.*, 1997; Zhaoxiang *et. al.*, 1996; Battisti *et. al.*, 1993)

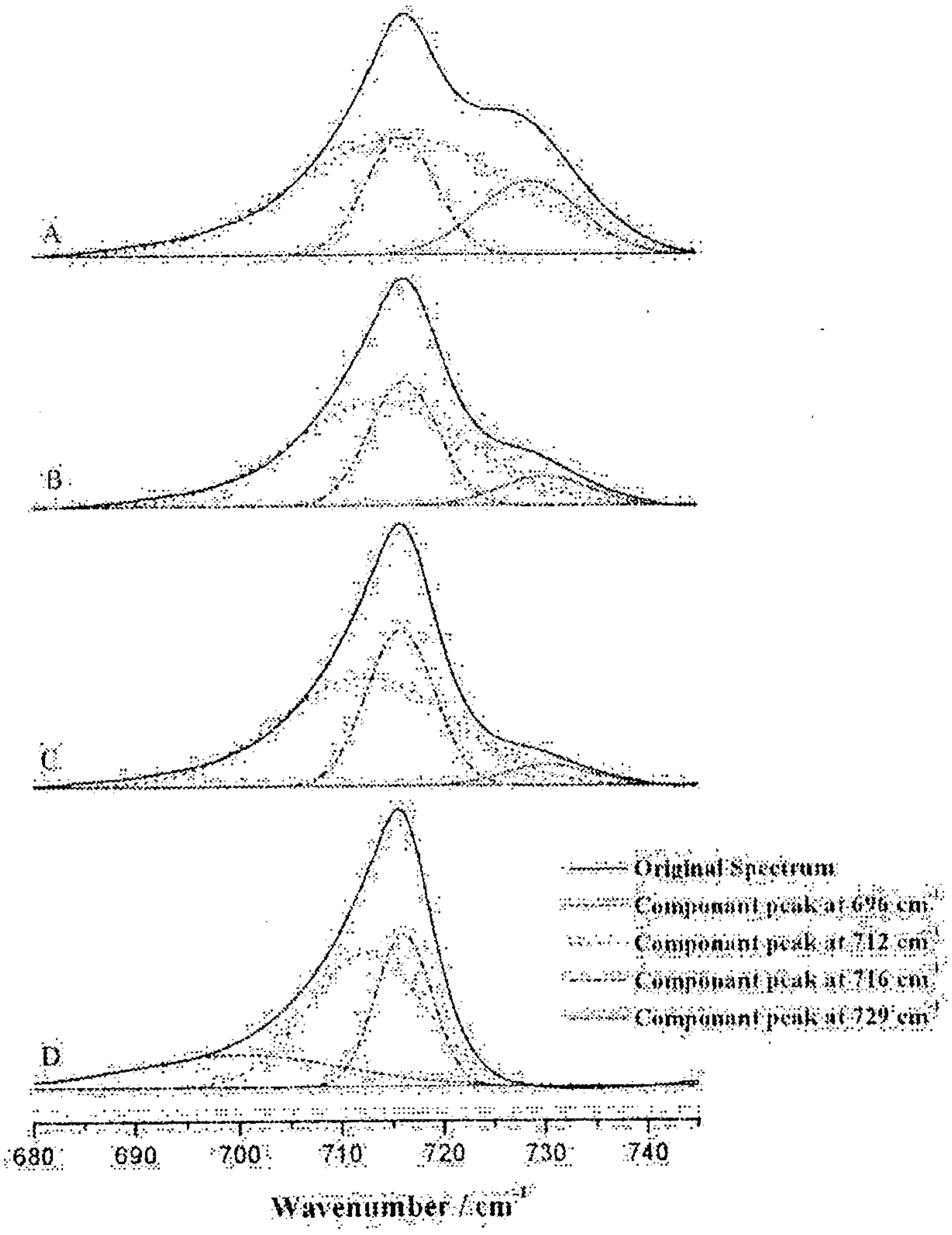


Figure 6: fitted curves for all the samples in the spectral range 680 cm^{-1} to 740 cm^{-1}

Table 4: Percentages of areas of each component peaks in the spectral range 680 cm^{-1} to 740 cm^{-1}

	712 cm^{-1}	716 cm^{-1}	729 cm^{-1}		893 cm^{-1}	903 cm^{-1}
			Area obtained from band fitting	Area calculated from 903 cm^{-1} peak		
A	61 %	21 %	18 %	18.1 % (67%/3.7)	33 %	67 %
B	60 %	29 %	11%	11.1 % (41%/3.7)	59%	41 %
C	57 %	34 %	9 %	8.6 % (32%/3.7)	68%	32 %
D	62 %	38 %	-	-	100%	-

The area of the peak at 712 cm^{-1} which corresponds to the symmetric ring deformation of PC does not vary much with the addition of the salt. But the area of the peak at 716 cm^{-1} which corresponds to the ring bending of EC is decreasing while the area of the peak at 729 cm^{-1} is increasing with the addition of the salt. This concludes Li is more prominent to interact with oxygen in the ring group of EC.

Similar band splitting phenomena was also observed in the mode corresponding to the ring breathing mode of EC (Fig 5 (b)). Here, the mother peak at 893 cm^{-1} was split into 893 cm^{-1} and 903 cm^{-1} with the increase of salt concentration. With the addition of 15% $LiBF_4$ to the composition *C*, a strong peak was observed around 903 cm^{-1} with a weak shoulder around 893 cm^{-1}. Peak fitted data is summarized in the Table 4. The percentage of peak area of the band at 903 cm^{-1} increase with the salt concentration and the percent area of the peak at 729 cm^{-1} is a factor of the percent area of the band at 903 cm^{-1} as given in the Table 4. This reveals that Li^+ is predominantly interacting with EC.

According to literature (Biying *et. al.*, 1996) EC has a pair of intense doublets at ~1770 cm^{-1} and 1798 cm^{-1} corresponding to C=O symmetric stretching mode. The position of these two peaks does not vary with the addition of PAN/ $LiBF_4$, but the peaks broadening can be observed. The band splitting towards the higher frequency level observed here should be accommodated strong interaction between the Li^+ ion of $LiBF_4$ and the oxygen atoms of the ring group (Figure 7) of plasticizers EC and PC (including both the C=O and C-O bonds).

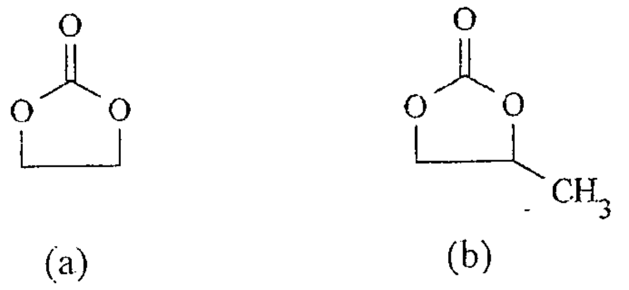


Figure 7: Chemical structure of (a) EC and (b) PC

5.0 Conclusions

In the present research work a PAN/$LiBF_4$/EC/PC gel polymer electrolyte system was studied. The maximum conductivity 4.25 × 10^{-3} S cm^{-1} was observed for the GPE sample contains highest salt concentration (composition *a*). However its mechanical stability was poor compared to the composition *b*. The filler (TiO_2) was improved the mechanical properties of the GPEs without significant reduction of the ionic conductivity. The prepared GPEs with and without filler were predominantly ionic conductors with negligibly small electronic conductivity. According to the FT-IR spectra of GPEs, the changes in the band shape, band width and vibrational frequencies indicated that there is strong interactions of L^+ ions of dissociated $LiBF_4$ with the ring and C=O group of the plasticizer molecules.

Acknowledgement

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ELECTRICAL AND FT-IR STUDY OF FUMED SILICA BASED GEL ELECTROLYTES; (TETRAGLYME)$_n$KIAND (ETHYLENE GLYCOL)$_n$KI

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Gel Electrolytes (GEs) are a newest generation of electrolytes, which exhibit high ionic conductivities at room temperature (RT) compared to solid electrolytes and good mechanical properties and long term stability compared to liquid electrolytes. Present days GEs have been identified as more promising electrolyte materials for various practical applications such as dye sensitized solar cells (DSSCs) and lithium ion rechargeable batteries. The emphasis of this work is on tetraethylene glycol dimethyl ether (tetraglyme), ethylene glycol (EG) and fumed silica based composite GE systems with potassium iodide (KI) as the salt. First, a series of liquid electrolytes were prepared by dissolving appropriate amounts of KI in EG and tetraglyme to obtain samples, (tetraglyme)$_n$KI and (EG)$_n$KI, with different O:I ratios (n = 12, 15, 20, 25, 30, 40, 50, 60 and 80). Then the GEswere formed by adding 10 wt. % of fumed silica. The highest ionic conductivity of 2.80×10^{-3} S cm^{-1} at RT, was observed for the gel electrolyte (tetraglyme)$_{15}$KIwith 10 wt. % fumed silica. The maximum conductivity of 1.50×10^{-2} S cm^{-1}at RT, was obtained for (EG)$_{12}$KI gel electrolyte system. The conductivity values of both gel systems studied are in the same order as the conductivities of corresponding liquid electrolytes. The data obtained from DC polarization tests verify that the prepared electrolytes are predominantly ionic conductors. The FT-IR spectra of both liquid and gel electrolyte systems based on tetraglymeindicate strong interactions present between K$^+$ ions and the ether oxygens of tetraglyme. The addition of the salt to EG shifts the O-H stretching mode to a higher wavenumber showing the strong interactions between EG and KI in both liquid and gel electrolyte systems.

Keywords:Gel electrolyte, tetraglyme, ethylene glycol, fumed silica, ionic conductivity, FT-IR

1. Introduction

The ever increasing energy demand requires more efficient, low cost, renewable energy sources. Alkaline batteries and solar cells play a major role in fulfilling the above need. Liquid electrolytes show high ionic conductivities and

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good performance in the above electrochromic devices compared to the solid electrolytes. However, there are a few inherit problems such assolvent vaporization, electrochemical corrosion and leakage with the use of liquid electrolytes. Gel electrolytes (GEs) have become promising materials for practical applications due to their valuable advantages over solid and liquid electrolytes. GEs exhibit comparably high ionic conductivities (> 10^{-3} S cm^{-1}) at room temperature compared to solid electrolytes[1, 2].

The present work focused on a gel electrolyte (GE) system formed by mixing low molecular weight organic solvents with fumed silica (SiO_2). Fumed silica has the ability to construct network structure in an organic media[3]. Fumed silica is formed by burning silicon tetrachloride ($SiCl_4$) in a flame of H_2 and $O_2$and as a result molten spheres of silicon dioxide are produced. Then these molten spheres are colliding and fuse with one another to form branched, three dimensional chains like aggregates. During the production process, hydroxyl groups tend to attach with the silicon atoms on the surface of the silica particles. These surface hydroxyl groups, called silanol groups (Si-OH), are able to make hydrogen bonds with suitable molecules. In the present study tetraethylene glycol dimethyl ether (or tetraglyme) and ethylene glycol (EG) were used as the organic solvents and potassium iodide (KI) was used as the salt to prepare GEs. The prepared electrolytes were characterized using AC impedance technique, DC polarization technique and FT-IR spectroscopy.

2. Experimental

Tetraglyme (Aldrich, 99%), ethylene glycol (99%), potassium iodide (KI) and fumed silica (SiO_2) (Aldrich, particle size 0.007 μ, surface area 390± 40 m^2 per gram) were used as the starting materials. Prior to use, SiO_2 was heated at 500 °C for 24 hours and KI was heated at 80 °C under vacuum for 24 hours. Tetraglyme and ethylene glycol was used as received.

2.1. Sample Preparation

A series of liquid electrolytes were prepared by dissolving appropriate amounts of KI in EG and tetraglyme to obtain samples, $(tetraglyme)_nKI$ and $(EG)_nKI$, with different O:I ratios (n = 12, 15, 20, 25, 30, 40, 50, 60 and 80). The mixtures of KI in EG and tetraglyme were stirred for 24 hours at room temperature and obtainedhomogeneous liquids.Then the composite gel was formed by adding the appropriate amount of fumed silica to achieve a filler concentration of 10 wt. %(*i.e.* 10% of the total weight of solvent (tetraglyme or EG) and KI).

2.2. Complex Impedance Spectroscopy

The ionic conductivity of the liquid electrolytes and GE samples were determined by the AC complex impedance technique with a computer controlled Solatron SI–1260 impedance analyzer in the frequency range 20 Hz –10 MHz.Impedance data of GEs weremeasured in the temperature range of 26°C to 65°C. For this gel electrolytes were smeared and sandwiched between two polished stainless steel blocking electrodes. For liquid electrolytes, a homemade glass holder was used with two polished stainless steel electrodes.

The ionic conductivity (σ) of the electrolyte samples were calculated using the Eq.(1):

$$\sigma = \frac{l}{R_b A} \tag{1}$$

where, $R_b$is the bulk resistance of the sample which was obtained from the graph of Z" (imaginary part of the impedance) vs. Z' (real part of the impedance), '*l*' is the thickness of the sample and '*A*' is the area of the sample.

2.3. DC Polarizing Technique

In order to determine the ionic nature of the prepared electrolyte samples, the DC polarizing technique was carried out. In this technique a small DC voltage ~1 V was applied across the sample and the DC current through the sample was noted down as a function of time. Stainless steel (SS) electrodes were used as blocking electrodes in the SS/GE/SS configuration; allowing only electrons to flow through an external circuit.

2.4 Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR studies were performed by using the Thermo Nicolet 6700 FTIR spectrometerin the wavenumber range from 600 cm^{-1}- 4000 cm^{-1} in order to determine the existence of the interactions between K^+ ion with the solvent (tetraglyme or EG) and fumed silica.

3. Results and discussion

3.1. DCPolarizing Technique

The Wagner's DC polarization test was performed for both liquid and gel polymer electrolytes[4]. This method was used to analyze the mobile species in the electrolyte. The DC current showed an abrupt drop within a short period of time for both liquid and gel samples due to the ion migration at the electrode electrolyte interface. After some time the current became constant which wasnegligible in magnitude, corresponding to the current due to electrons. According to our data it can be concluded that both liquid and gel electrolyte samples are predominantly ionic conductors with negligibly small electronic conductivity.

3.2. Complex Impedance Spectroscopy

The ionic conductivities of the liquid electrolytes with different O:I molar ratios at room temperature for both systems,(Tetraglyme)$_n$KI and (EG)$_n$KI,are depicted in Figure 1 (a) and Figure 1(b) respectively.The highest ionic conductivity of 3.78×10^{-3} S cm^{-1}for (Tetraglyme)$_n$KIliquid electrolyte system was obtained at room temperature for the electrolyte sample with O:I molar ratio of 20:1. Further increase of salt {i.e. in (Tetraglyme)$_{15}$KI and (Tetraglyme)$_{12}$KI samples} reduces the ionic conductivities, presumably due to formation of large aggregate ions. The ionic conductivities of the liquid electrolytes of (EG)$_n$KI system, with different O:I molar ratios at room temperature are depicted in the Figure 1(b). The highest ionic conductivity of 2.01×10^{-2} S cm^{-1} was obtained at room temperature for the electrolyte sample with O:I molar ratio of 12:1.

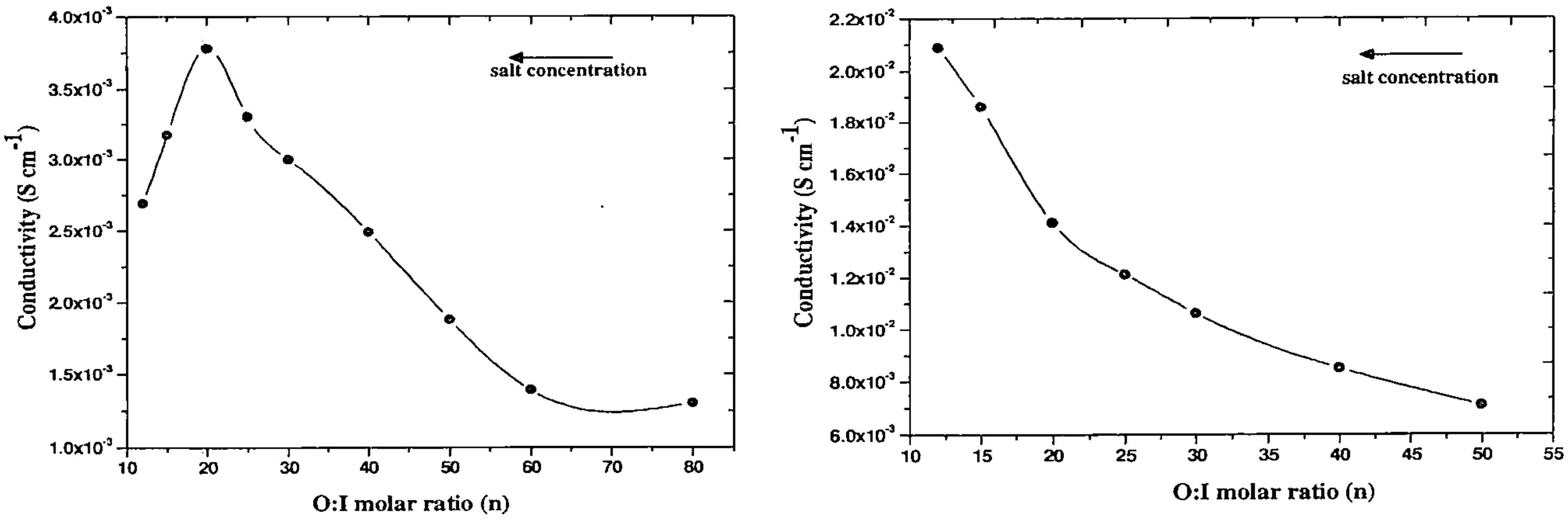

Figure 1: The ionic conductivities of the liquid electrolytes with different O:I molar ratios (a) (Tetraglyme)$_n$KI system (b) (EG)$_n$KI system.

Then preheated fumed silica was added as 10 wt. %of the total weight of tetraglyme or ethylene glycol and KI to the liquid electrolytes with different molar ratios to form GEs. Figure 2 shows the temperature dependence of the ionic conductivities of prepared GEs.

Within the tested temperature range, the conductivity variation of all GEs well obeys the Arrhenius relationship[5].

$$\sigma T = \sigma_0 \exp\left[\frac{-E_a}{kT}\right] \qquad (2)$$

whereE_a is the activation energy, σ_0 is the pre-exponential factor, k is the Boltzmann constant and T is the absolute temperature.

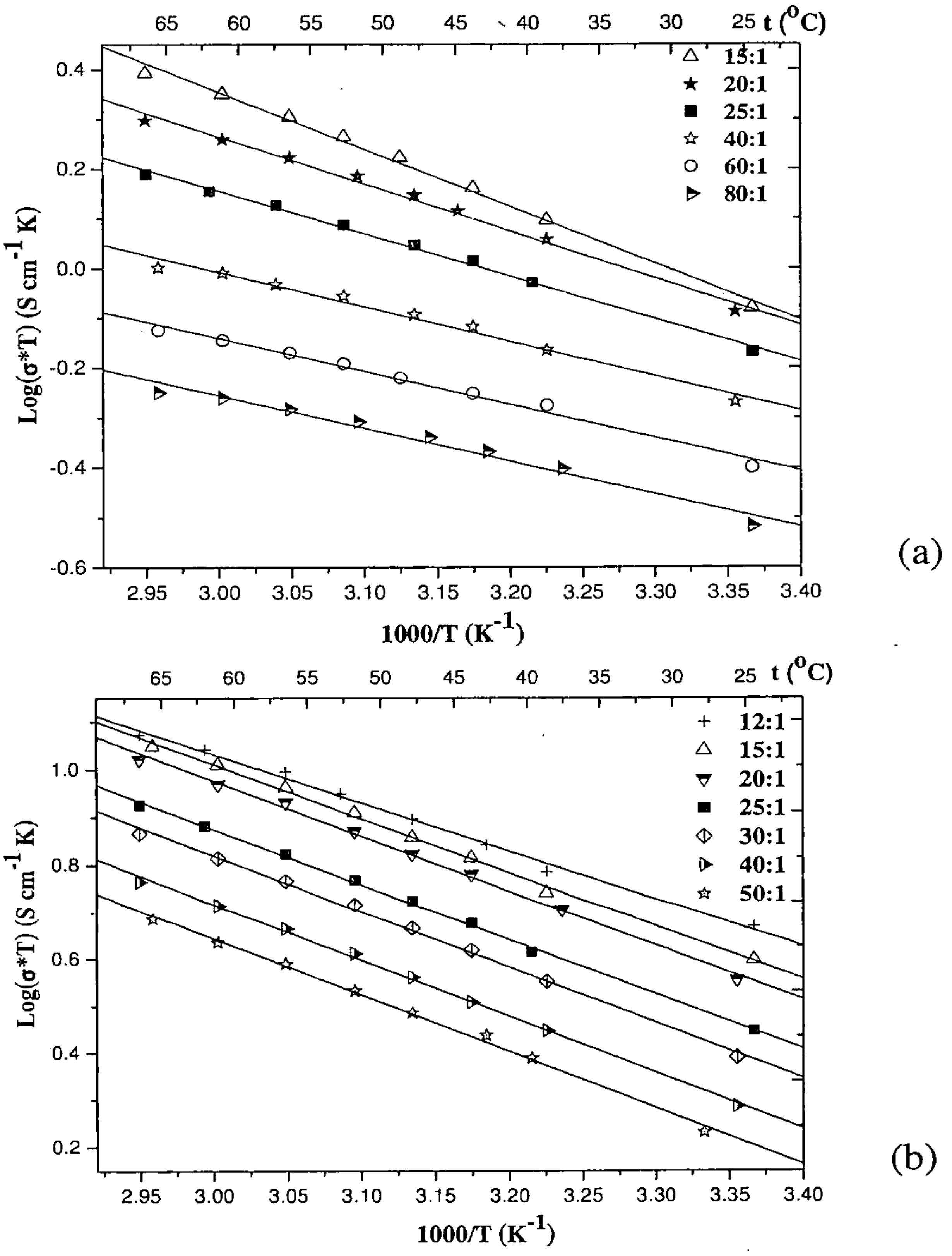

Figure 2. The ionic conductivities of the GEs with 10wt. % SiO_2 with different O:I molar ratios (a) $(Tetraglyme)_nKI$system (b) $(EG)_nKI$ system

As shown in Figure 2(a), after addition of fumed silica to $(\text{Tetraglyme})_n\text{KI}$ liquid electrolytes to form gels, GE with 15:1 molar ratio exhibits the highest ionic conductivity of 2.80×10^{-3} S cm^{-1}, which is higher than the ionic conductivity of the 20:1 gel electrolyte sample. In the 15:1 gel electrolyte sample, the aggregate formation may be hindered by the addition of fumed silica.

For $(\text{EG})_n\text{KIGE}$ system, 12:1 molar ratio exhibits the highest ionic conductivity of 2.01×10^{-2} S cm^{-1}. However, the ionic conductivity has been slightly reduced after the addition of silica in both GE systems. This may occur due to the blocking of the motion of salt ions.

In these systems fumed silica with surface silanol groups (Si-OH) was used as the gelation agent. The main driving force to form a gel is believed to be the hydrogen bond between silanol groups on adjacent silica molecules or hydrogen bonds between silanol groups of silica molecules and ether oxygen of tetraglyme molecules. Raghavan*et.al* has discussed in detail about three factors to interpret the possible mechanisms responsible for the stability of these silica gel systems. They are electrostatic interactions, van der Waals forces and solvation phenomenon. According to the findings of Raghavan*et.al,* electrostatic interactions and van der Walls forces play a negligible role and have no correlation for the network formation of these GE systems. So they suggest that a different mechanism, i.e. solvation phenomena due to hydrogen bonding, is affecting the gel formation of these systems[6].

In solvation phenomena, if the solvent possess high hydrogen bonding capacity, there will be hydrogen bonds formed between solvent molecules and surface silanol groups of silica particles. As a result, a solvation layer is formed around the silica particles. If the solvent possess low hydrogen bonding capacity, hydrogen bonding between surface silanol groups of neighbor silica particles can be more prominent to form a "gel"[6].

Among the two systems studied, ethylene glycol has high hydrogen bonding capacity than tetraglyme. Therefore, we believe that the interactions between silica surface groups is the most dominant driving force for the gelation process for $(\text{Tetraglyme})_n\text{KI}$system and the interactions between silica surface groups and ethylene glycol is the most dominant driving force for the gelation process for $(\text{EG})_n\text{KI}$system.

3.3. FT-IR Measurements

In the present paper the vibrational spectroscopy has been used to study the interactions between the cation and the solvent.Considering the cation interactions with other possible species in this GE, there can be two possibilities. First, the K^+ ion can form direct links with the ether oxygens from separate solventmolecules which restrict the motion of the solventmolecules or K^+ ion can attach to the ether oxygen of a single solvent molecule. In the second possibility, K^+ ions may bridge the surface silanols of the fumed silica and ether oxygens of the solvent molecules. In our study, evidence for the interactions between K^+ ion and the solvent molecules could be found.

3.3.1. Tetraglyme based GE system

In the FT-IR spectra in Figure 3 (a), bands between 800 cm^{-1} and 900 cm^{-1} have been assigned to modes of CH_2 wagging and C-O-C stretching motions[7]. FT-IR spectra of tetraglyme gel without KI and liquid tetraglyme show a band centered at wavenumber 850 cm^{-1} and with the increasing salt concentration a weak shoulder is appearing at around 862 cm^{-1}. This weak shoulder is assumed to be due to the CH_2 wagging and CH_2 twisting motions of C-O-C-C-O-C units which are interacting with the K^+ ions.

In Figure 3(b), the band appearing at the wavenumber 1098 cm^{-1} of liquid and gel tetraglymeis assigned to the vibrational mode of CH_2 wagging[7]. With the addition of the KI salt this peak is showing a downshift to wavenumber 1085 cm^{-1} for the gel electrolytewith 15:1 molar ratio. This indicates the K^+ interactions with ether oxygens of tetraglyme.

FT-IR spectra of gel and liquidtetraglyme and $(Tetraglyme)_nKI$ (n = 80, 20 and 15)gel electrolytes with different O:I molar ratios at room temperature in the range of wavenumbers 1310 cm^{-1} – 1410 cm^{-1} spectral region is shown in Figure 3(c). As seen in the spectrum of pure tetraglyme and $(Tetraglyme)_nKI$gel electrolytes, a weak shoulder is appearing in the range of wavenumbers 1310 cm^{-1} – 1410 cm^{-1}spectral region with the addition of salt. The band appearing at 1350 cm^{-1} in tetraglyme has been assigned for CH_2 rocking[8]. With the addition of the salt to the tetraglyme, the band has split further to give an additional component at around ~1359 cm^{-1}.

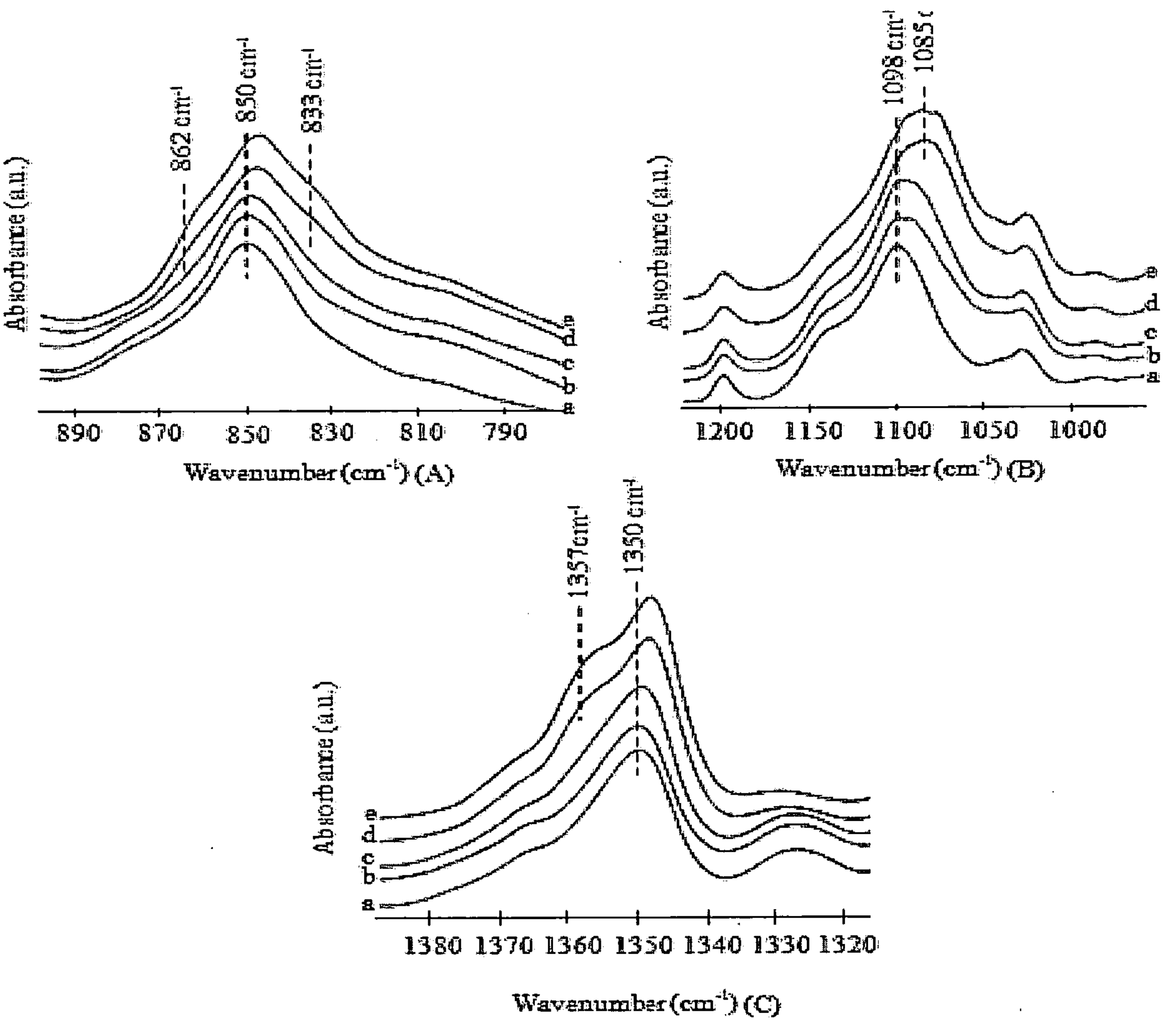

Figure 3: FT-IR spectra of a-liquid tetraglyme, b-gel tetraglyme (tetraglyme+ fumed SiO_2), c-$(Tetraglyme)_{80}KI$ GE, d- $(Tetraglyme)_{20}KI$ GE and e- $(Tetraglyme)_{15}KI$ GE at room temperature in the (A) 780 cm^{-1} – 890 cm^{-1} spectral region (B) 950 cm^{-1} – 1220 cm^{-1} spectral region (C) 1320 cm^{-1} – 1390 cm^{-1} spectral region.

3.3.2. Ethylene glycol based GE system

The Table 1 gives the vibrational frequencies of CH_2 rocking,CH_2 wagging, CH_2 twisting and C-O stretching modes of liquid and gel ethylene glycol without KI and gel electrolyte, $(EG)_{12}KI$, (i.e. n = 12). Coordination of K^+ions with the oxygen atoms of EG molecules has influenced the peak positions of the above modes of EG. Each peak is shifting by about 5 to 7 cm^{-1}. The C-C stretching vibration mode of pure ethylene glycol is located at 861 cm^{-1} wavenumber[9]. Its position remains unchanged with the addition of the salt. This indicates that the K^+ ions are interacting with both oxygen atoms of ethylene glycol, without disturbing to the symmetry of the EG molecule.

Table 1: FT-IR assignments of ethylene glycol[9].

Assignment	**Wavenumber (cm^{-1})**	
	Peak positions of pure EG	**When interact with K^+ ion**
C-C Stretching	861 *m*	861
CH_2 Rocking	882 *s*	877
C-O Stretching	1084 *vs*	1079
CH_2 Twisting	1205 *mb*	1198
CH_2 Wagging	1257 *wb*	1251

b= broad, *vs*= very strong, *s*= strong, *w*= weak, *m*= medium

As shown in the Figure 5, the interaction of K^+ ion and oxygen atoms of ethylene glycol has been influenced to O-H stretching mode causing a shift of the peak position. O-H stretching mode of pure EG (liquid and gel) is a broad band centered at around 3300 cm^{-1}wavenumber[9]. As the salt concentration is increased, the centre of the peak is shifted towards higher wavenumbers as shown in Figure 5.

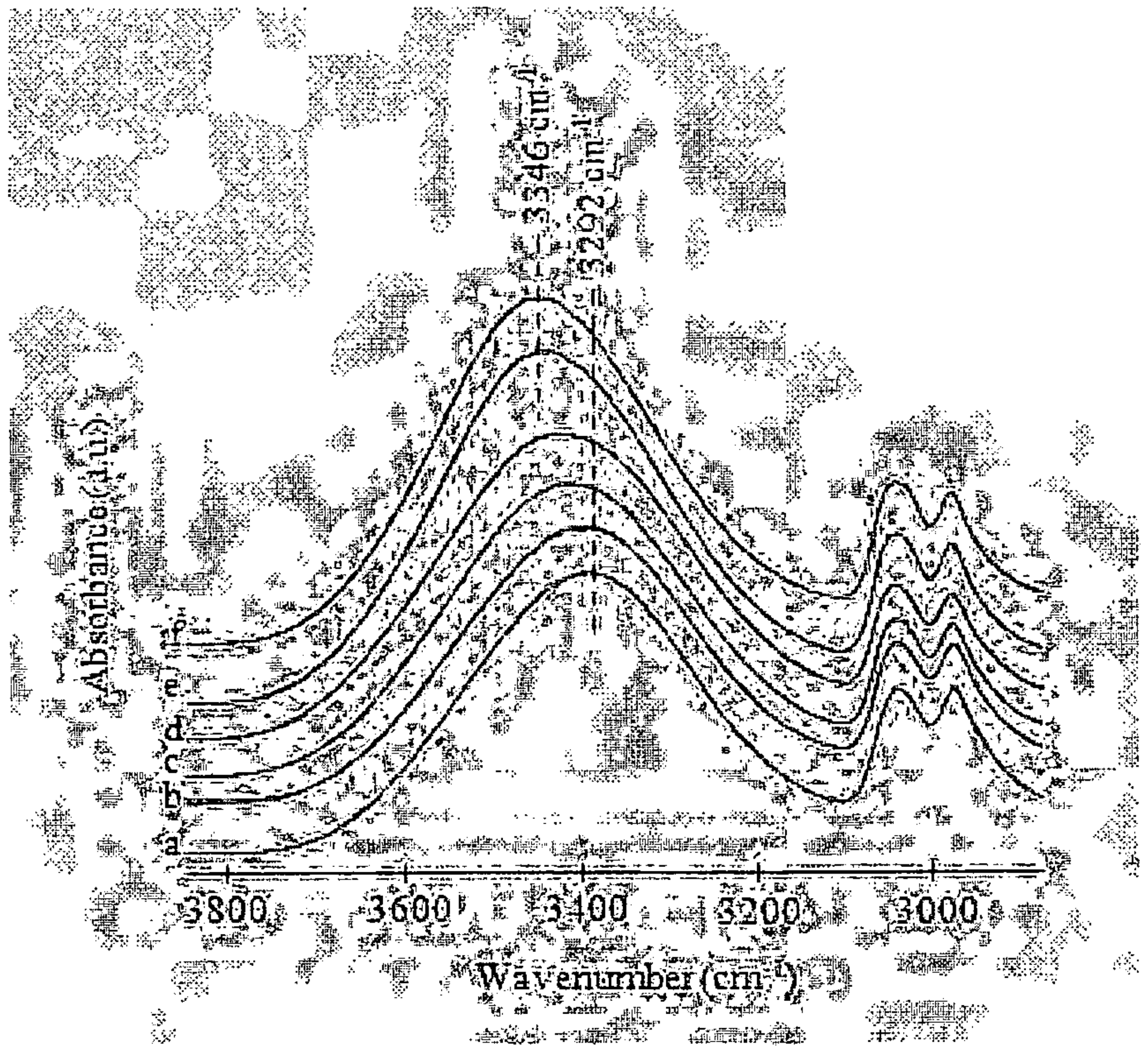

Figure 5: O-H stretching mode of,a-liquid EG, b-gel EG (EG+ fumed SiO_2), c- $(EG)_{50}KI$ GE, d- $(EG)_{30}KI$ GE, e- $(EG)_{15}KI$ GE and f- $(EG)_{12}KI$ GE systems at roomtemperature.

4. Conclusions

By mixing low molecular weight tetraglyme or ethylene glycol and KI based liquid electrolyte, with fumed silica, gel electrolytes has more stability compare to liquid electrolytes successfully fabricated. The prepared GEs were predominantly ionic conductors. The addition of fumed silica to liquid electrolyte forms a gel without a significant drop of ionic conductivity. The highest ionic conductivity of 2.80×10^{-3} S cm^{-1} was observed for the tetraglyme based GE of O: I molar ratio of 15:1 with 10 wt. % fumed silica. For ethylene glycol based GE system, the highest ionic conductivity 2.01×10^{-2} S $cm^{-1}$was observed for the electrolyte at 12:1 molar ratio. According to the FT-IR spectra of liquid electrolytes, the changes in the band shape and vibrational frequencies indicated that there are strong interactions of K^+ ions of dissociated KI with the ether oxygen of tetraglyme and ethylene glycol chains.

Acknowledgements

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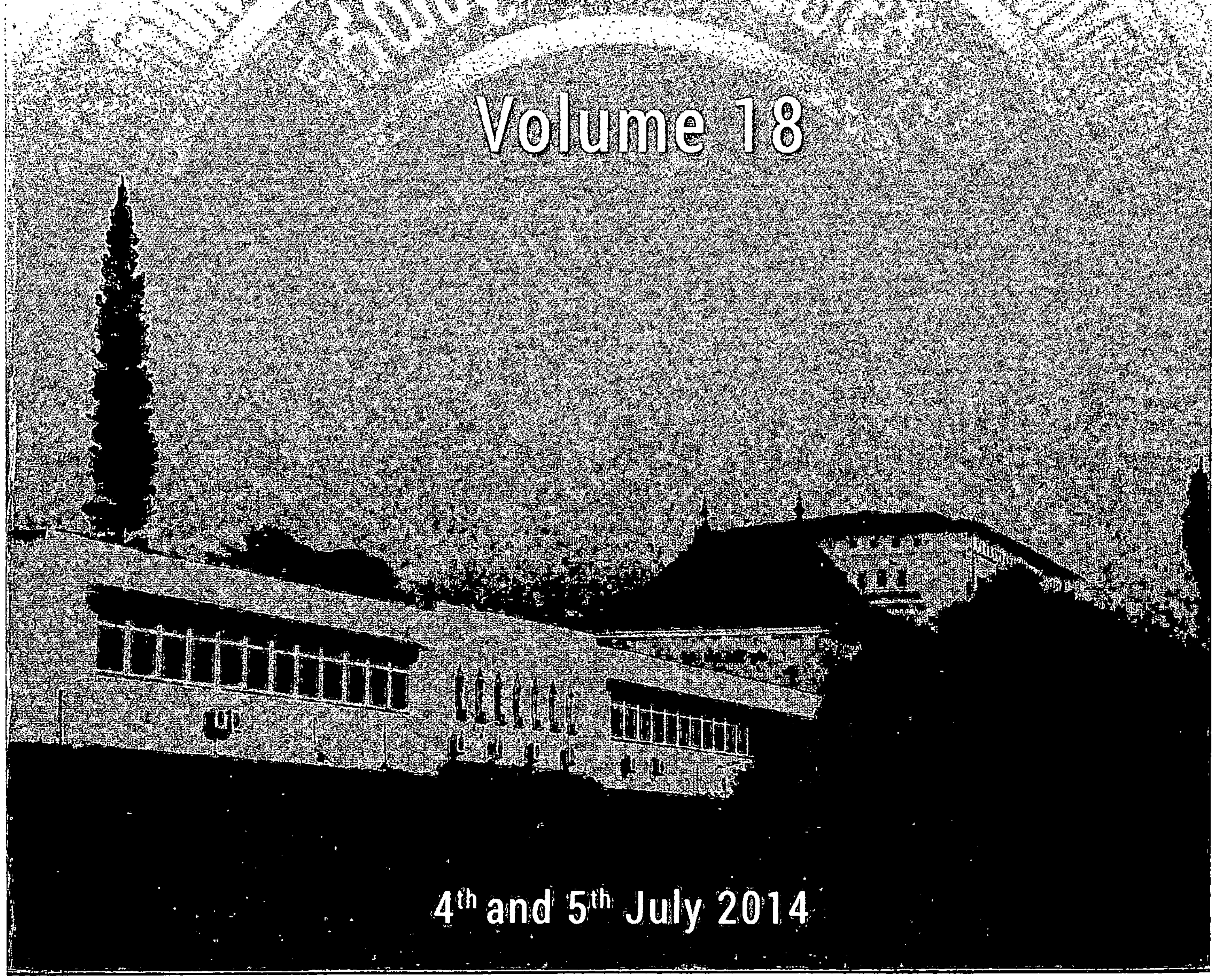

4th and 5th July 2014

Abstract No: 511 **Natural Sciences**

EFFECT OF ILMENITE AS A FILLER IN THE POLYMER ELECTROLYTE $(PEO)_{20}LITF$

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Polymer electrolytes have potential applications in lithium rechargeable batteries, fuel cells, supercapacitors, electrochromic displays and photo-electrochemical solar cells. In this work we have studied the effect of ilmenite as a filler in a polymer electrolyte based on poly(ethylene oxide) and the salt, lithium trifluoromethanesulfonate. Ilmenite is a titanium bearing mineral which is naturally available in Sri Lanka. The average particle size of ilmenite sample used to fabricate the composite polymer electrolyte (CPE) was 418 nm. X-Rays Fluorescence spectra (XRF) show that ilmenite contains 65% of Ti and 35% of Fe in the form of oxide. Polymer electrolytes,$(PEO)_mLiTf$ (m=10,20,30,40,50,60,70, and 80), and composite polymer electrolytes, $(PEO)_{20}LiTf$ + x wt.% ilmenite and $(PEO)_{20}LiTf$ + x wt.% TiO_2 (x = 10,15) were prepared using solvent casting technique. The resulting CPEs have been characterized by complex impedance spectroscopy, X-ray diffraction, polarized light microscopy and DC polarization test. Room temperature conductivities of the filler free samples are about 10^{-7} S cm^{-1}, and highest conductivity was obtained for the $(PEO)_{10}LiTf$ sample. Addition of ilmenite has enhanced the ionic conductivity in an order of magnitude in the CPE with 15 wt. % of ilmenite. Reduction of the spherulites size and decrease in the intensity of the PEO peaks of XRD spectra were observed. This shows that the incorporation of ilmenite has reduced the crystalline nature and enhanced the fraction of the amorphous phase of the polymer electrolyte facilitating the ion conductivity. Commercially available TiO_2 and ilmenite show very similar performance in CPEs.

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IONIC CONDUCTIVITY AND FT-IR STUDY OF TETRAGLYME/KI/ FUMED SILICA GEL POLYMER ELECTROLYTE

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The Gel Polymer Electrolytes (GPEs) are promising materials for the ever-growing need for high energy density power sources such as lithium ion rechargeable batteries and dye sensitized solar cells. The use of GPE, which carrying both cohesive properties of solid and diffusive properties of liquid, overcomes many practical problems that solid and liquid electrolytes causes. They exhibit high ionic conductivities at room temperature (RT) and good electrode-electrolyte interfacial property than with solid electrolytes, and long term stability than that of liquid electrolytes. Most of the previous research works were focused on GPEs with plasticizers, such as ethylene carbonate (EC) and propylene carbonate (PC), as the gelation agents. The emphasis of this work is on tetraethylene glycol dimethyl ether (tetraglyme), potassium iodide (KI) and fumed silica based GPE system without any plasticizer. The composite GPEs were formed by adding appropriate amount of fumed silica to the liquid electrolytes prepared with different O:I ratio. In this case, the fumed silica was added as a percentage to the total weight of tetraglyme and the salt KI. The maximum ionic conductivity of 3.78×10^{-3} S cm^{-1} was obtained for the liquid electrolyte with O:I molar ratio 20:1. The ionic conductivities of fumed silica added GPSs with different O:I ratio are also in the order of $\sim10^{-3}$ S cm^{-1} at RT. The highest ionic conductivity of 2.80×10^{-3} S cm^{-1} at RT was observed for the GPE sample with O:I molar ratio 15:1, incorporated with 10 wt.% fumed silica. However, the gel electrolytes showed slightly reduced ionic conductivity at RT, compared to the liquid electrolytes. This may occur due to the hindrance caused by the silica to the motion of polymer chains. The DC polarization test verified that the prepared electrolytes were predominantly ionic conductors. In this system, the main driving force to form a gel is believed to be the hydrogen bond between silanol groups on adjacent silica molecules or the hydrogen bonds between silanol groups of silica molecules and ether oxygen of tetraglyme molecules. FT-IR studies were carried out to investigate the form of interaction between the K^+ ions with the ether oxygen of tetraglyme. Many vibrational frequency modes have been identified to verify that the addition of the salt changes the conformation of the polymer tetraglyme which leads to changes in the FT-IR spectra of each liquid electrolyte.

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