



Synthesis Characterization and Dielectric Properties of PVA/F 127 block copolymer blend polymer electrolyte for PSSC application

Supriya Dhumal¹, , Arun Patil¹, Nitin A. Jadhav*², Amit Saxena³, Chandrakant Dighavkar¹

¹L.V.H. College, Panchavati, Nashik(M.S.), India

²Vidya Pratishthans Kamalnayan Bajaj Institute of Engineering and Technology Baramati

³Department of Physics Shri Vaishnav Institute of Science SVV, Indore 453111

Summary: In this paper we studied and firstly we synthesized for combination of three different material like PVA, F-127 and KI with different quantity. We did the characterization for the prepared solid polymer films. For the prepaid solid polymer blend we studied connection or we can say relationship between ionic and electrical transport. We find out the impedance values for all prepared solid polymer films. Based on that impedance information we can conclude that we have got maximum conductivity value which is 8.2891×10^{-4} at (60/40) wt %. These parameters like dielectric occurrence, mobility and diffusion coefficient triggers the conductivity data.

Keywords: PVA; KI and I2; solid polymer.

Introduction:

Now a days Free standing solid polymer is one of the most popular and interesting subject. Mostly we can use these in different applications for different purpose. We can say different applications not only in solar cell but also super capacitor and hybrid power sources.^[1-6] Solid polymer strongly appears a one of the appropriate alternatives for electrochemical tool package, despite the fact that liquid contract in gel pores, it produces trouble and eventually gets the poor performance. Liquid electrolyte has different drawback not only evaporation and thermal stability but also it release harmful gas which is very dangerous for human heath as well as environment. In current years, solid polymers have fascinated well known consideration due to their such a lot of high-quality properties together which includes just like liquid conductivity (10^{-2} to 10^{-4}

S/cm),^[7-9] that's considered necessary for growing any electrochemical gadgets. The research of mobility ought to be completed to improve the conductivity. Experimenters are trying hard to find a good high ionic conductivity polymer. So far no one has been able to fully understand the ionic conductivity operation in solid polymer. That is why it is necessary to understand this important ionic mechanism movement which is based on polymer relaxation action. From this paper we have prepared a new solid polymer electrolyte by mixing KI with blend of PVA and F-127. In this we change the temperature of PVA from 100⁰ to 120⁰ C. PVA is very easy to use and available at a very low cost and does not require any expensive instruments.^[10-12] Electrolyte is a very important part in PSSC. Electrolytes are of different types such as solid, liquid and gel. Among these, liquid electrolyte is the most efficient electrolyte, but at the same time, its problem is that it does not last for a long time, it dries up with some period of time. Gel polymer electrolyte in now a days very good and reliable because of these factors like not only long term stability but also better ionic conductivity and good thermal stability. It is also have good compatibility with TiO₂ electrode. In solar cell we can make solar cells by using different types of polymer electrolyte like PAN, PMMA, F-127, PVDF etc. All these types of polymers can be used with different salts to carry maximum ions. In our solar cell study, we have used two polymer blend, PVA and F-127 and provided an in depth look at them. We have used PVA and F-127 in our study because it has many advantages such as easy to manufacture, low cost, high electrical conductivity and most importantly it is very environmental stable. Combination of PVA and F- 127 is expected to give us better properties. On the plus side, f-127 is readily soluble in most solvent PVA is a nontoxic polymer that forms very good free standing solid film. Detailed information about PVA can be obtained by different characteristic techniques like XRD, DSC. There is no report on the utilization of F-127-PVA-blended GPEs in Perovskite sensitized solar cell available from the literature. A mixture of both PVA and F-127 produces a good material, as the resulting material become very good and high electric conductive. Both PVA and F- 127 are mixed by electrochemical method. The polymer made by this method exhibits very good conductive and mechanical properties. PVA has high hydrogen bonding due to which the polymer chain shows a regular morphology. PVA is an artificial polymer so it dissolves in water. PVA and F-127 polymer electrolyte have good polarity along with good mechanical strength. Due to mixing with the host polymer, the physical properties of the conducting polymer are improved in terms of flexibility and electrical conductivity.^[25] A mixture of PVA and F-127 is prepared using solution cast technique. In this work, we have tried to prepare a new conducting polymer by using these two polymers, so we will get very cheap and high efficient material which will be very useful for making perovskite solar cell. In this

mixture we have used f-127 and PVA in the ration of 60:40 to make our solid polymer electrolyte. Our aim is to see how the number of mobility, density and diffusion coefficient of both these polymers affect the performance of PSSC.

1. Experimental procedure:

Preparation of polymer electrolyte:

Double distilled water, methanol are used as solvent to make polymer electrolyte. PVA polymer was dissolved in double distilled water and F-127 and KI were dissolved in methanol, all these chemicals were used from Aldrich, USA. All the dissolved chemicals solutions were collected together by solution cast method and then we made solid polymer film from it.

Sample Result and Discussion

1. Results and discussion :

1.1 Conductivity measurement

Use the formula below to determine the ionic conductivity of these 16 samples:

$$\sigma = G \times l/A \quad (1)$$

Where l is the sample thickness, A is the test-ready area of the sample, G is the conductivity ($G=1/R_b$), R_b is the apparent resistance on the real axis of the Nyquist plot, σ is the ionic conductivity, and l is the thickness of sample.

Table 1. Solid polymer electrolyte systems' ionic conductivity at room temperature.

Composition(wt % of KI)	σ (S/cm)
90	6.4494×10^{-8}
80	8.12499×10^{-5}
70	1.8034×10^{-4}
60	8.28×10^{-4}
50	2.1586×10^{-4}
40	2.1186×10^{-4}
30	1.7455×10^{-4}

20	2.2586×10^{-8}
10	3.6911×10^{-6}

The ionic conductivity of all 16 samples calculated and written in the above table 1. When we add KI to the polymers PVA and F-127, the ionic conductivity of the polymer increases and the increased conductivity is highest at 60%wt. of KI. Where the conductivity value approaches at sample (4) i.e. 8.28×10^{-4} S/cm it decrease after that. For the calculation we apply the frequency in between 100Hz to 1MHz, temperature same as room temperature. As more KI is added, the ionic conductivity and number of mobile charge carriers increases, but if the KI concentration exceeds 60wt %, the ionic conductivity decreases. The conductivity measured solid film thickness ranged from 0.012 to 0.030 cm and the impedance measured solid polymer film area range from 1.77 to 2 cm².

The ionic conductivity for electrolytic systems is:

$$\sigma = n : q : \mu \quad (2)$$

Where n is the carrier density, q is the carrier charge and μ is the carrier mobility. Therefore, increasing the parameter n or q will definitely distress the ionic conductivity value.

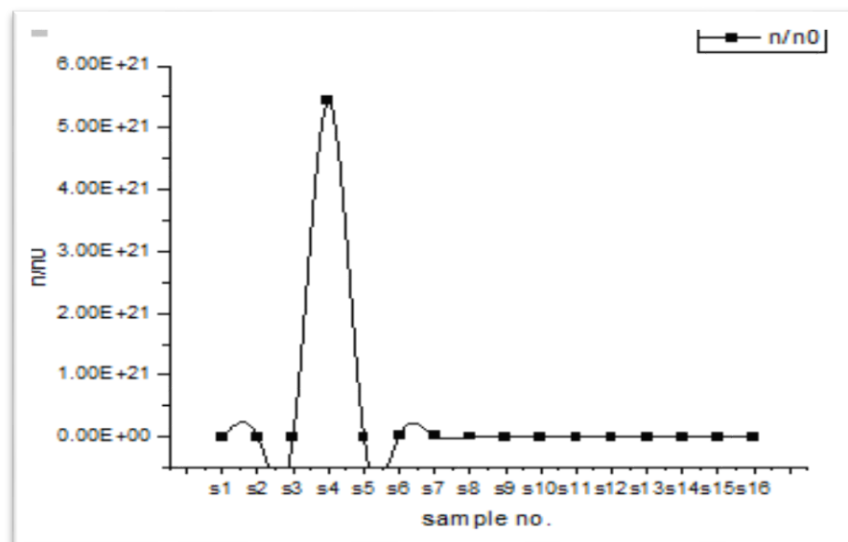
1.2 Ion dissociation factor:

The carrier concentration can be stated as follows, in accordance with the electrolytic dissociation theory:

$$n = n_0 \exp(-U/2\epsilon kT) \quad (3)$$

ϵ is the permeability of the system, U and k are the Boltzmann constant, and the temperature dissociation energy T of the sample salt.

From table 1 we will know what the role of charge carriers is in solid polymer of impedance measurement values. Using all 16 samples, we can calculate the relationship between the total number of charge carriers and room temperature. 3.35 eV is the dissociation energy of KI. With the addition of KI to the polymer concentration, Figure 1 depicts the shift in the relative quantity of charge carriers. Relative number of charge carriers is high up to KI 60% wt doping limit and then it



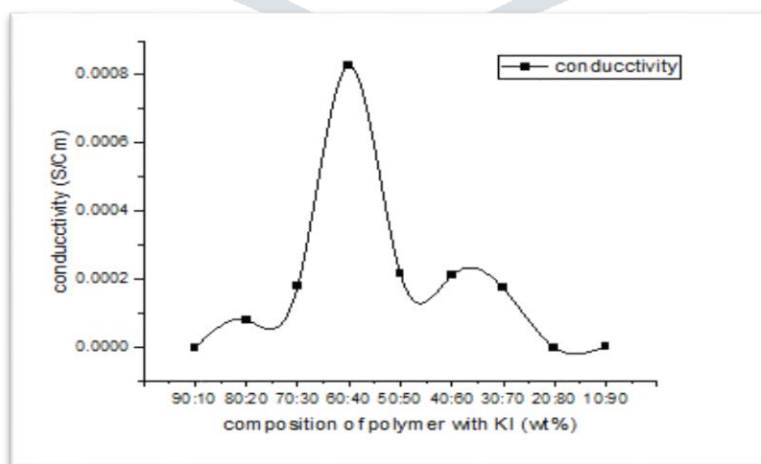
starts to decrease slowly.

Figure 1. Changes in the number of carriers in the polymer matrix of PVA and f-127 saturated solid electrolyte solution with increasing KI content.

The figure 1 demonstrates how the quantity of charge carriers has a major impact on the conductivity of KI matrix solid polymers. [18-19]

1.3 Dielectric studies:

Variations of a few nanometers at the molecular level have a direct effect on the dielectric, and with this study we can obtain detailed information about the various molecular motions and slower processes in the sample. Figure 2 shows the dielectric constants of all samples at 100 kHz.



When KI is added to a polymer, the electrolyte matrix's dielectric constant is altered. Low frequencies produce the maximum value of the dielectric constant, which causes a quantitative shift in the free carriers as well as the electrical conductivity.

We used data from complex impedance spectroscopy to determine the electrical modulus and transmittance after making more thorough experimental observations of the transition behavior, ion transport mechanism, and dielectric characteristics. The conductance behavior of ions in solid polymer electrolytes is studied using the dielectric study of solid polymer electrolytes, which is highly helpful and significant. The ionic conductivity formulated as:

$$\varepsilon^* = \varepsilon' + i\varepsilon''$$

$$|\varepsilon^*| = \sqrt{\varepsilon'^2 + \varepsilon''^2}$$

The displacements of ε' and ε'' for KI salt compositions from 10 to 90 mass % are shown in Fig. 3(a) and Fig. 3(b), respectively. ε' and ε'' were deliberate using the equations:

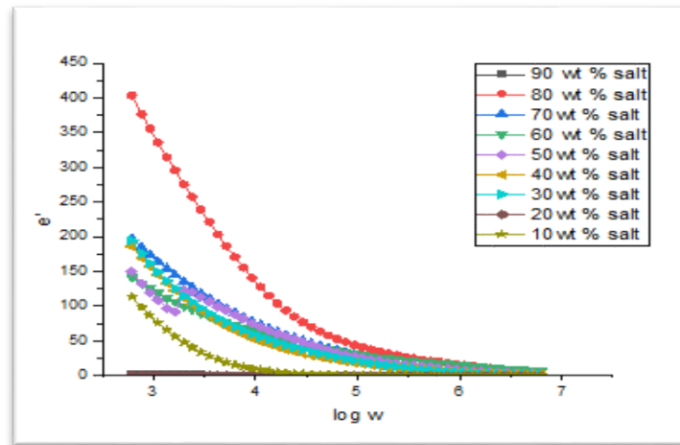
$$\varepsilon' = \frac{-Z''}{\omega C (Z'^2 + Z''^2)}$$

$$\varepsilon'' = \frac{-Z'}{\omega C (Z'^2 + Z''^2)}$$

$$C = \frac{\varepsilon_0 A}{L}$$

where z' and z'' are the real and imaginary parts of the resistance, C is the capacitance of the empty measuring cell, w is the pulse, A is the area, ε_0 is the dielectric constant and L is the thickness of the solid polymer film. The behavior of the graphs is similar in that there is a sharp increase at low frequencies and a gradual decrease at high frequencies. This is the result of polarization.

(a)



(b)

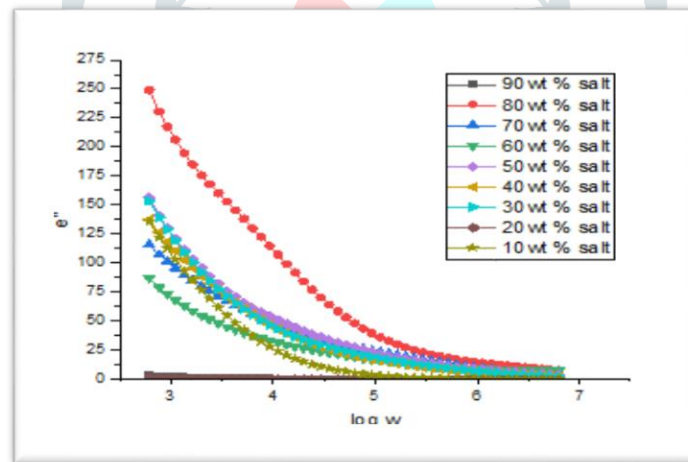


Figure 3. (a) Real part of the dielectric constant (ϵ_0) variation with frequency for various composition concentrations in weight percent of KI salt (b) and imaginary dielectric constant (ϵ'') loss variation with frequency for various composition concentrations in weight percent of KI salt at room temperature.

1.4 Dielectric loss tangent :

We have determined the tangential loss in the manner shown below in order to better understand the phenomenon of insulation and conductive behavior:

$$\tan \delta = \frac{\epsilon''}{\epsilon'}$$

where ε' and ε'' are the real and imaginary parts of the dielectric constant of the solid polymer electrolyte. The attenuation is still calculated for different frequencies and components as shown in the figure 4. It has the highest conductivity of any other combination, which is also corroborated by the conductivity data, and has greater bumps at higher frequencies. Figure 4 shows the variable frequency shear damping of F-127 and KI films at different concentrations at room temperature. The loss spectra are characterized by peaks observed in the frequency characteristics of the F-127 and KI films, indicating the presence of long dipoles in the solid polyelectrolyte films. The frequency of relaxation depends on the characteristics of bipolar relaxation. As the KI concentration increased, the transverse damping peak shifted to a higher frequency, and the conductance peak gradually decreased, reaching 60% of the KI mass concentration. With the exception of KI the amorphous content of the substance is believed to have increased. Dielectric expansion is observed in the dielectric loss map due to the orientation of the electrode array. The obtained regeneration phenomenon corresponds to the dielectric regeneration time $\gg 1.33 \times 10^{-7}$ s for 60% KI.

$$T = \frac{1}{2\pi f_{max}}$$

where f_{max} is the peak frequency and T is the dielectric recovery time.

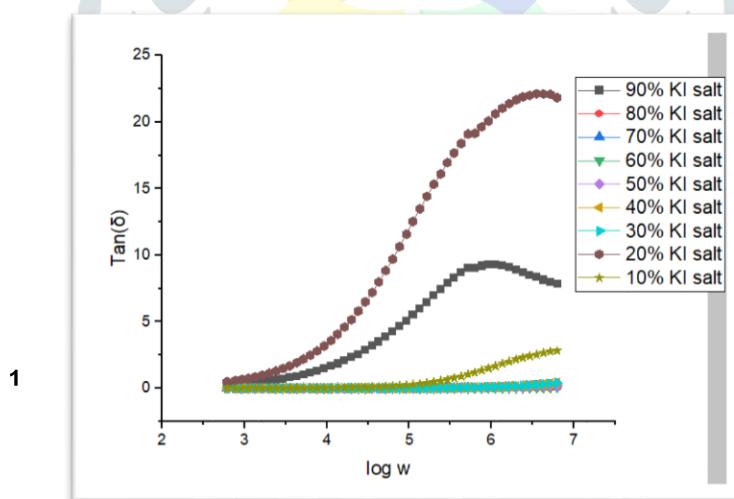


Figure 4. Tangent losses were estimated for various KI salt concentrations at room temperature using various frequencies.

1.5 Dielectric modulus:

In solid polymer electrolyte systems, the dielectric modulus has been estimated and examined for various recovery events. ^[18] The data ε^* can be converted into the formula M^* according to the following relation:

$$M^* = \frac{1}{\epsilon^*} = M' + M''$$

$$|M^*| = \sqrt{M'^2 + M''^2} \tag{8}$$

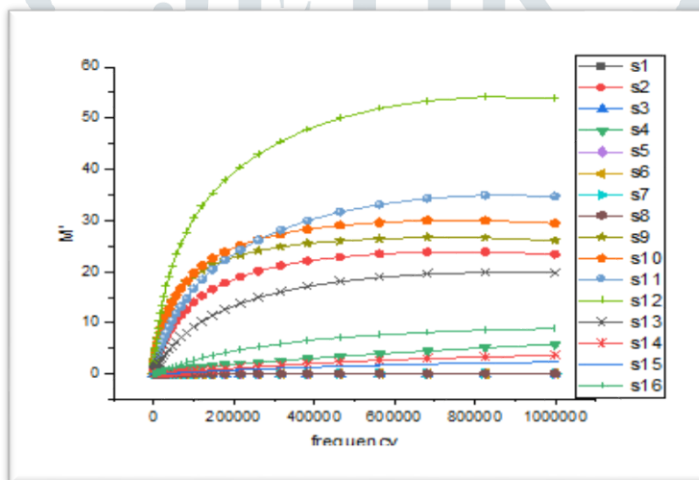
where

virtual dielectric coefficient M' and real dielectric M'' :

$$M' = \frac{\epsilon'}{[(\epsilon')^2 + (\epsilon'')^2]}$$

$$M'' = \frac{\epsilon''}{[(\epsilon')^2 + (\epsilon'')^2]}$$

(a)



(b)

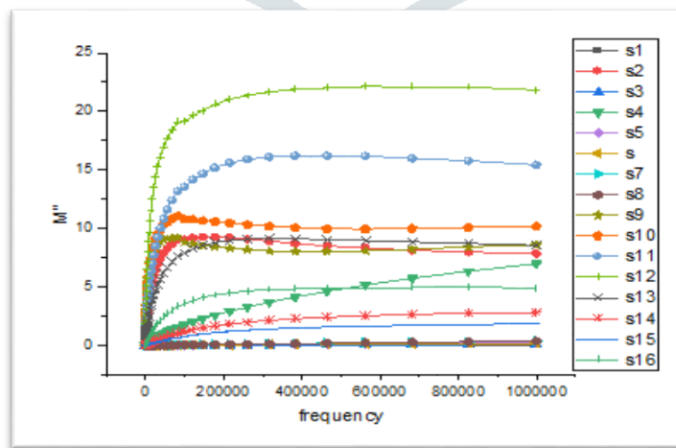


Figure 5. (a) Real component (M') of the dielectric device at various frequencies and KI concentrations (b) imaginary part (M'') at various polymer concentrations at various frequencies. Using polymer electrolyte F-127 at room temperature, various KI systems.

2. Conclusions:

We were successful in creating solid PVA, F-127, and KI polymer electrolyte membranes. With is KI doping, complex impedance spectroscopy revealed improved ionic conductivity that peaked at 60% wt% of KI salt. The maximum dielectric loss is seen at low KI frequency concentrations, which is caused by electrode polarization. Electrical conductivity is governed by an increase in the overall number of charge carriers. As a result, the free mobile charge carriers indicated in the dielectric data are responsible for the increase in ionic conductivity. The conductance mode is also followed by n/n_0 measurements.

References:

- [1] Gray FM. Solid polymer electrolytes. New York (NY): VCH Publishers; 1991.
- [2] MacCallum JR, Vincent CA. Polymer electrolyte review. London: Elsevier Science Publishers Ltd.; 1987 and 1989. 1 and 2.
- [3] Kaneko M, Hoshi T, Kaburagi Y, Ueno H. Solid type dye-sensitized solar using polysaccharide containing redox electrolyte solution. *J Electroanal Chem.* 2004;572: 21_27.
- [4] Bacto agar-based gel polymer electrolyte. *Ionics.* 2012;18:359_364.
- [5] Kubo W, Kitamura T, Hanabusa K, Wada Y, Yanagida S, Quasi-solid-state dye-sensitized solar cells using room temperature molten salts and a low molecular weight gelator. *Chem Comm.* 2002;4:374_375.
- [6] Osada Y, Kajiwara K. Gels handbook: function. San Diego (CA): Academic Press; 2001.
- [7] Singh VK, Annu A, Singh U, Singh P, Pandey SP, Bhattacharya B, Singh PK. Dye sensitized solar cell based on poly(vinyl alcohol) doped with ammonium iodide solid polymer electrolyte. *J Opto electron Adv Mater.* 2013;15:927_931.
- [8] Sekhon SS, Singh HP. Ionic conductivity of PVDF-based polymer gel electrolytes. *Solid State Ionics.* 2002;152_153:169_174.
- [9] Bhattacharya B, Lee JY, Geng J, Jung HT, Park JK. Effect of cation size on solid polymer electrolyte based dye-sensitized solar cells. *Langmuir.* 2009;25:3276_3281.
- [10] Finkenstadt VL. Natural polysaccharides as electroactive polymers. *Appl Microb Biotechnol.* 2005;67:735_745.

- [11] Singh R, Jadhav NA, Majumder S, Bhattacharya B, Singh PK, Novel biopolymer gel electrolyte for dye-sensitized solar cell application. *Carbohydr Polym.* 2013;91:682_685.
- [12] Khanmirzaei MH, Ramesh S. Ionic transport and FTIR properties of lithium iodide doped biodegradable rice starch based polymer electrolytes. *Int J Electrochem Sci.* 2013;8:9977_9991.
- [13] Grätzel M (2003) Dye-sensitized solar cells. *J Photochem Photobiol C: Photochem Rev* 4(2):145–153
- [14] Bach U, Lupo D, Comte P, Moser JE, Weissortel F, Salbeck J, Spreitzer H, Gratzel M (1998) Solid-state dye-sensitized mesoporous TiO₂ solar cells with high photon-to-electron conversion efficiencies. *Nature* 395(6702):583–585
- [15] Wu JH, Lan Z, Lin JM, Huang ML, Hao SC, Sato T, Yin S (2007) A novel thermos setting gel electrolyte for stable quasi-solid-state dye sensitized solar cells. *Adv Mater* 19(22):4006–4011
- [16] Chen C-L, Teng H, Lee Y-L (2011) In situ gelation of electrolytes for highly efficient gel-state dye-sensitized solar cells. *Adv Mater* 23(36) :4199–4204
- [17] Rika AA, Rahman MYA, Salleh MM (2009) Preparation and characterization of PAN based solid polymeric electrolyte for dyesensitized solar cells. *Phys B Condens Matter* 404(8–11):1359–1361
- [18] Anandan S, Pitchumani S, Muthuraaman B, Maruthamuthu P (2006) Heteropolyacid-impregnated PVDF as a solid polymer electrolyte for dye-sensitized solar cells. *Sol Energy Mater Sol Cells* 90(12):1715–1720
- [19] Theerthagiri J, Senthil RA, Buraidah MH, Madhavan J, Arof AK (2015) Effect of tetrabutylammonium iodide content on PVDF/PMMA polymer blend electrolytes for dye-sensitized solar cells. *Ionics* 1(10):2889–2896
- [20] Theerthagiri J, Senthil RA, Ali@Buraidah MH, Madhavan J, Mohd Arof AK (2015) Studies of solvent effect on the conductivity of 2-mercaptopyridine- doped solid polymer blend electrolytes and its application in dye-sensitized solar cells. *J Appl Polym Sci* 132(35):42489
- [21] Chen K-F, Liu C-H, Huang H-K, Tsai C-H, Chen F-R (2013) Polyvinyl butyral-based thin film polymeric electrolyte for dye sensitized solar cell with long-term stability. *Int J Electrochem Sci* 8:3524–3539
- [22] Kang J, Li W, Wang X, Lin Y, Xiao X, Fang S (2003) Polymer electrolytes from PEO and novel quaternary ammonium iodides for dye-sensitized solar cells. *Electrochim Acta* 48(17):2487–2491
- [23] Tiautit N, Puratane C, Panpinit S, Saengsuwan S (2014) Effect of SiO₂ and TiO₂ nanoparticles on the performance of dye-sensitized solar cells using PVDF-HFP/PVA gel electrolytes. *Energy Procedia* 56(0):378–385
- [24] Wang X, Zhang Y, Xu Q, Xu J, Wu B, Gong M, Chu J, Xiong S (2015) A low-cost quasi-solid DSSC assembled with PVDF-based gel electrolyte plasticized by PC-EC & electrodeposited Pt counter electrode. *J Photochem Photobiol A Chem* 311:112–117
- [25] Ren Y, Zhang Z, Fang S, Yang M, Cai S (2002) Application of PEO based gel network polymer electrolytes in dye-sensitized photoelectron chemical cells. *Sol Energy Mater Sol Cells* 71(2): 253–259.
- [26] Yang H, Huang M, Wu J, Lan Z, Hao S, Lin J (2008) The polymer gel electrolyte based on poly(methyl methacrylate) and its application in quasi-solid-state dye-sensitized solar cells. *Mater Chem Phys* 110(1):38–42

- [27] Aram E, Ehsani M, Khonakdar HA (2015) Improvement of ionic conductivity and performance of quasi-solid-state dye sensitized solar cell using PEO/PMMA gel electrolyte. *Thermochim Acta* 615:61–67
- [28] Arof AK, Aziz MF, Noor MM, Careem MA, Bandara LRAK, Thotawatthage CA, Rupasinghe WNS, Dissanayake MAKL (2014) Efficiency enhancement by mixed cation effect in dyesensitized solar cells with a PVdF based gel polymer electrolyte. *Int J Hydrog Energy* 39(6):2929–2935
- [29] Higashino T, Imahori H (2015) Porphyrins as excellent dyes for dye-sensitized solar cells: recent developments and insights. *Dalton Trans* 44:448
- [30] Sandoval C, Castro C, Gargallo L, Radic D, Freire J (2005) Specific interactions in blends containing chitosan and functionalized polymers. Molecular dynamics simulations. *Polymer* 46(23):10437–10442.
- [31] Kuila T, Acharya H, Srivastava SK, Samantaray BK, Kureti S (2007) Enhancing the ionic conductivity of PEO based plasticized composite polymer electrolyte by LaMnO₃ nanofiller. *Mater Sci Eng B* 137(1–3):217–224
- [32] Jia Y-T, Gong J, Gu X-H, Kim H-Y, Dong J, Shen X-Y (2007) Fabrication and characterization of poly (vinyl alcohol)/chitosan blend nanofibers produced by electrospinning method. *Carbohydr Polym* 67(3):403–409
- [33] Yang C-C, Wu GM (2009) Study of microporous PVA/PVC composite polymer membrane and its application to MnO₂ capacitors. *Mater Chem Phys* 114(2–3):948–955
- [34] Joge P, Kanchan DK, Sharma P, Nirali G (2013) Effect of nanofiller on electrical properties of PVA-PEO blend polymer electrolyte. *India J Pure Appl Phys* 51:350
- [35] Abd El-kader FH, Hakeem NA, Elashmawi IS, Ismail AM (2013) Structural, optical and thermal characterization of ZnO nanoparticles doped in PEO/PVA blend films. *Aust J Basic Appl Sci* 7(10): 608–619
- [37] Kapil M, Lata S (2013) A review: residual solvents and various effective gas chromatographic techniques in the analysis of residual solvent. *Int J Pharm Res Rev* 2(10):25–40
- [38] Rajendran S, Babu RS, Sivakumar P (2007) Effect of salt concentration on poly (vinyl chloride)/poly (acrylonitrile) based hybrid polymer electrolytes. *J Power Sources* 170(2):460–464
- [39] Arof AK, Naeem M, Hameed F, Jayasundara WJMJSR, Careem MA, Teo LP, Buraidah MH (2014) Quasi solid state dye-sensitized solar cells based on polyvinyl alcohol (PVA) electrolytes containing I⁻/I⁻³ redox couple. *Opt Quant Electron* 46(1):143–154
- [40] Ramya CS, Selvasekarapandian S, Hirankumar G, Savitha T, Angelo PC (2008) Investigation on dielectric relaxations of PVP– Ionics