# Effect of Binary salt based Gel Polymer Electrolytes on Dye Sensitized Solar Cells

A. Pathirana, Y.M.C.D. Jayathilake, K. Perera* and K. Vidanapathirana
*Department of Electronics, Wayamba University of Sri Lanka, Kuliyapitiya*
**kumudu31966@gmail.com*

## ABSTRACT

This paper reports about the use of a binary salt based gel polymer electrolyte (GPE) for dye sensitized solar (DSS) cells. The two salts are Tetrapropylammonium Iodide ($Pr_4NI$) and Zinc Iodide ($ZnI_2$) which has not been considered commonly. The GPEs consist with Polyacrylonitrile (PAN) as the polymer and Ethylene Carbonate (EC)/ Propylene Carbonate (PC) as the solvents. Preparation of the electrolyte films were done using hot pressed method. AC impedance data were gathered to study the conductivity values. DC polarization tests were done to find the nature of conductivity. All GPEs are having satisfactory conductivity values and are proven to be good ionic conductors. DSS cells were fabricated in the configuration, FTO (Fluorine doped Tin Oxide) electrode / $TiO_2$ / Dye / GPE / Pt / FTO. A lower cell performance was observed from the cell having $ZnI_2$ based GPE. It could be improved noticeably by adding equal amount of $Pr_4NI$.

## 1. INTRODUCTION

Due to the rapid increment of the demand for energy during last couple of decades and also with the reduction of fossil fuel supply every year, searching alternative energy sources has become a must. In that situation, solar energy has been identified as a very suitable alternative solution as it is clean, abundant and most of all renewable [1]. Today, conversion of solar energy directly into electricity has received a tremendous attention of researchers all over the world. As a result, several types of solar cells have been introduced to the world with positive and negative points. Dye sensitized solar (DSS) cells belong to one generation and its original model was reported by O'Regan and Gratzel [2]. DSS cells generally consist with a nano porous Titanium dioxide ($TiO_2$) electrode coated with a dye for light harvesting, an electrolyte having iodide / triiodide based redox couple to regenerate photo excited dye molecules and a platinum coated counter electrode. Liquid electrolytes have been employed for many DSS cells but they have undergone many problems such as poor long term stability, leakage, photochemical degradation and corrosion [3]. Therefore, there has been a great enthusiasm towards gel polymer electrolytes to be applied for DSS cells in recent past [4, 5]. Among them, most of the studies are based on one type of iodide salt preferably with a larger cation [6, 7]. Recently, an intense interest has arose using binary salt based GPEs for DSS cells as it was discovered that mixing up of a larger cation based iodide salt and a high charge density cation based iodide salt effectively enhance the cell performance [8]. Key objective of the present study is investigating the performance of a DSS cell when fabricated using a $ZnI_2$ based GPE. $ZnI_2$ has been employed for this purpose because it has not been highly considered for DSS cell applications.

## 2. EXPERIMENTAL

### 2.1 Preparation of the Gel Polymer Electrolytes

Polymethylmethacrylate (PMMA – ALDRICH), Ethylene Carbonate (EC – ALDRICH), Propylene Carbonate (PC – ALDRICH), Tetrpropylammonium Iodide ($Pr_4NI$ – ABCR), Zinc Iodide ($ZnI_2$ – ALDRICH) and Iodine ($I_2$ – Breckland Scientific Supplies) were used as received. The compositions as well as the preparation conditions of the gel polymer electrolytes were chosen as reported by us in a previous study [9].
Compositions of the three samples have been given in the Table 1.

Table 1: Compositions of the samples in weight basis

| Composition | Sample |
|---|---|
| 40 $ZnI_2$ / 20 PMMA / 30 EC / 30 PC / 3% $I_2$ | A |
| 20 $Pr_4NI$+20 $ZnI_2$ / 20 PMMA / 30 EC / 30 PC / 3% $I_2$ | B |
| 40 $Pr_4NI$ / 20 PMMA / 30 EC / 30 PC / 3% $I_2$ | C |

### 2.2 AC Conductivity Measurements of the Samples

Circular shape pellets from each sample were cut and assembled in spring loaded brass sample holders which are sealed by means of an O ring. Thickness as well as diameter of each pellet were measured using a micrometer screw gauge. AC impedance measurements were taken from room temperature to 45 $^0$C in the frequency range 0.01 Hz to 0.1 MHz with a Metrohm M101 impedance analyzer. The sample holder was kept inside a glass tube furnace to change the temperature and the temperature was measured by a digital thermometer. Data analysis was carried out using Non Linear Least Square Fitting Method (NLLS).

### 2.3 DC Polarization Tests

In order to identify the nature of conductivity, DC polarization tests were done with stainless steel blocking electrodes under a bias potential of 1 V. For that, circular shape samples were loaded in side brass sample holders. Current variation of the samples with time was observed at room temperature. A digital multimeter was used to measure the current.

### 2.4 Fabricating and Characterizing DSS Cells

Fluorine doped Tin Oxide (FTO) glass strips were cleaned well using detergents and distilled water. Titanium Dioxide ($TiO_2$) paste was prepared by grinding $TiO_2$ (Degussa P-25) initially for few minutes alone. Then, few drops of Acetic acid and Ethanol were added while grinding. This was spread on an active area of 1 $cm^2$ on FTO glass strips using doctor blade method. Sintering was done at 450 $^0C$ for 45 minutes. Those nano porous electrodes were allowed to cool down to room temperature. They were then dipped in ethanolic Ruthenium dye solution for dye absorption for 24 hours. DSS cells in the configuration, $FTO/TiO_2$/Dye/Gel polymer electrolyte/Pt/FTO were assembled using each of the gel polymer electrolyte sample. The photo current – voltage characteristics of the cells were measured under 100 W illumination.

## 3. RESULTS AND DISCUSSION

### 3.1 Impedance Data Analysis

From the high frequency intercept in the impedance plot, the bulk electrolyte resistance was determined. Ionic conductivity was calculated using the equation

$$\sigma = (1/R_b)t/A \qquad \text{……………….(1)}$$

where $\sigma$ – ionic conductivity
$R_b$ – bulk electrolyte resistance
T – thickness of the electrolyte film
A – area of cross section of the electrolyte film

This process was done for each measured temperature and for each sample.

### 3.2 Temperature Dependence of Conductivity

Fig. 1 shows the conductivity variation with inverse temperature for all three samples.

It is very clear that conductivity increases with temperature due to the fact that ions in the systems get more energy and hence their motion increase resulting conductivity increment as per the relationship,

$$\sigma = ne\mu \qquad \text{……………..(2)}$$

where n – the charge carrier concentration
e – charge of an electron
$\mu$ – ion mobility

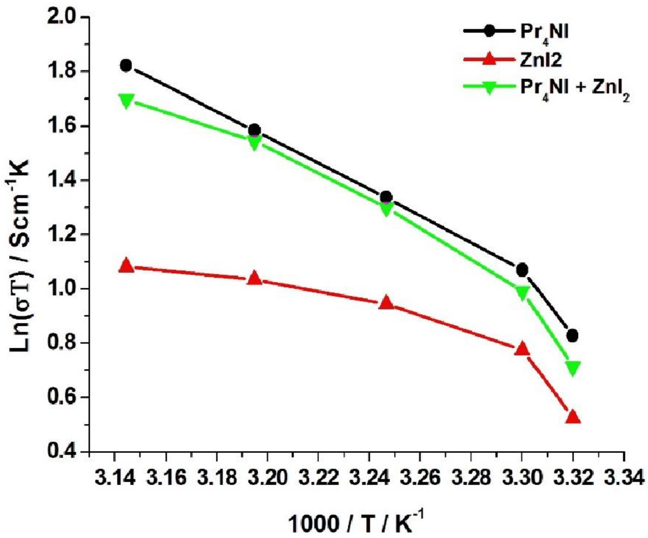



Fig. 1: Temperature dependence of conductivity of the three samples

$ZnI_2$ based gel polymer electrolyte does have a lower ionic conductivity throughout the temperature range considered. It may be due to the fact that Zn and $I^-$ ions are not free enough to move as Zn and $I^-$ may have coupled strongly due to the divalency of Zn.

Room temperature conductivities of the three systems are shown in Table 2. All the systems are having appreciable conductivity values in the order of $10^{-3}$ which is considerable for applications.

Table 2: Room temperature conductivity value of the three gel polymer electrolyte systems

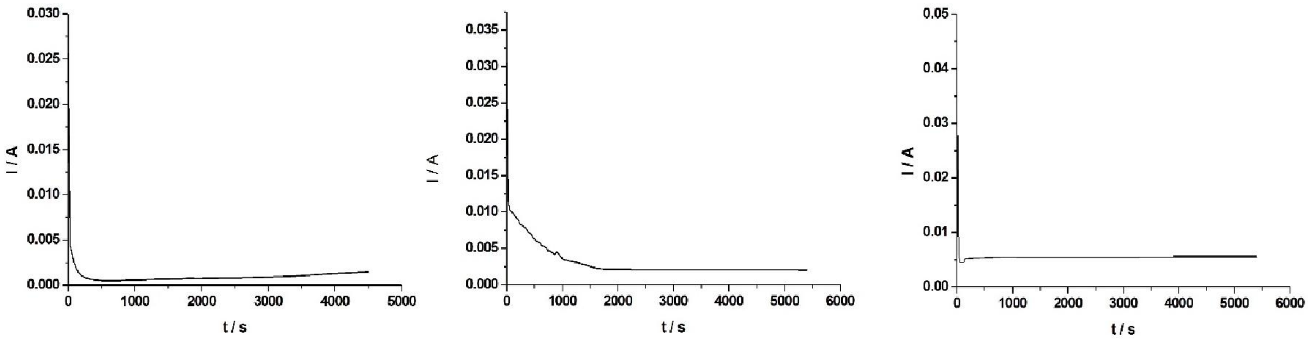
| System | $\sigma_{RT} \times 10^{-3}$ / $Scm^{-1}$ |
|---|---|
| A | 5.61 |
| B | 6.78 |
| C | 6.87 |

### 3.3 DC Polarization Tests

Fig. 2(a), Fig. 2(b) and Fig. 2(c) illustrate the DC polarization curves for the three systems studied. The ionic transference numbers were calculated as

$$t_i = t_{total} - t_{saturated} / t_{total} \quad \ldots\ldots\ldots\ldots(3)$$

Here, $t_i$ is ionic transference number.




2(a) 2(b) 2(c)

Fig. 2: DC polarization results corresponding to current variation with time for the cell configuration stainless steel (SS) electrode / Gel Polymer electrolyte / stainless steel (SS) electrode. 2(a) - $Pr_4NI$ system ti = 0.98, 2(b) - $ZnI_2$ system ti = 0.93 and 2(c) - Mixed system ti = 0.92.

The resultant ionic transference numbers of the gel polymer electrolytes are comparatively equal and the values are high enough to prove that systems are predominantly ionic conductors. The value of 0.98 in the $Pr_4NI$ based gel polymer electrolyte becomes the highest value among them. In that system, the two types of ions are $Pr_4N^+$ and $I^-$. It has been reported by many researchers that due to the large size of $Pr_4N^+$, it is less mobile [10]. By our observation, it can be concluded that $I^-$ ions are more responsible for the higher ionic transference number. In the gel polymer electrolyte consisting with the binary salt mixture, it can expect a high transference number due to the presence of many ions. But, the result of 0.92 is closer to $ZnI_2$ based GPE suggesting that hindrance of ionic contribution for transference number measurements. Sometimes, it may be due to any interaction between the two cations, the contribution may be coming only from $I^-$.

### 3.4 Performance of DSS cells

When light falls on dye via photo anode, it gets excited. Then the photo excited dye transfers an electron to the semiconducting $TiO_2$ via electron injection. It is then transported through $TiO_2$ and collected by FTO glass. That electron travels through the external circuit.

$$Dye + Light \rightarrow Dye^* \text{.........................} (4)$$

$$Dye^* \rightarrow e^- (TiO_2) + Oxidized\ dye \text{.........} (5)$$

The triiodide / iodide redox couple in the electrolyte undergoes reduction at counter electrode and regeneration of the oxidized dye also takes place in a nano second range.

$$(1/2)I_3^- + e- \rightarrow (3/2)I^- \text{.....................................} (6)$$

$$Oxidized\ dye + (3/2)I^- \rightarrow Dye + (1/2)I_3^- \text{.............} (7)$$

[1, 11]

Photo current – voltage characteristics were measured under constant illumination for all three cells and also repeated investigations were done to check the reproducibility.

Open circuit voltage (Voc), short circuit current density (Jsc), fill factor (ff) and efficiency values ($\eta$) are given in Table 3 for each cell.

Fill Factor, ff = Pmax / Voc.Isc , where P max refers to maximum power
Efficiency, $\eta$ = Isc.Voc.FF / Pin, where Pin refers to incident power.

Fig. 3 and Table 3 show the photo current-voltage characteristics and parameters obtained for the solar cells using three different gel polymer electrolytes respectively.

Table 3: Solar cell parameters of the three different cells

| | Voc / mV | Jsc / mAcm$^{-2}$ | ff / % | $\eta$ / % |
|---|---|---|---|---|
| Cell A | 357 | 0.29 | 56.33 | 0.88 |
| Cell B | 467 | 0.37 | 63.39 | 1.65 |
| Cell C | 629 | 2.25 | 42.91 | 9.22 |

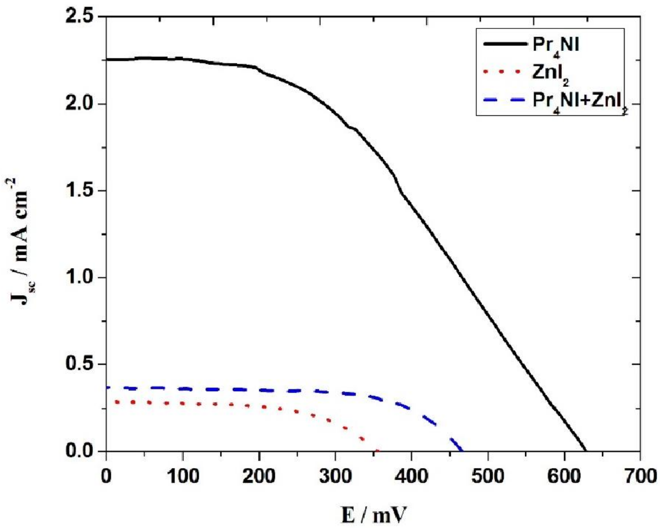



Fig. 3: Photo current-voltage characteristics of the three different types of solar cells

One clear feature in the performance is that $ZnI_2$ based DSS cell exhibits lower performance than the other two. Lower $J_{sc}$ value of $ZnI_2$ based DSS cell may be due to its low ionic conductivity though it is in $10^{-3}$ order [12]. A possible higher resistance for ion migration may retard the supply of $I_3^-$ to the Pt electrode. This may result in lowering $I_3^-$ supply and also reduces the dye regeneration and hence the decrement of $J_{sc}$ may take place. When compared with conductivities and performance characteristics of three cells, it is obvious that other than conductivity, there may be several factors that govern cell performance.

Due to the large size of $Pr_4N^+$, its mobility may be low and hence, iodide conduction in $Pr_4NI$ based GPE may be high. This may result in higher efficiency in $Pr_4NI$ based cell. It is seen that performance of DSS cells based only on $ZnI_2$ could be improved upon addition of $Pr_4NI$.

## 4. CONCLUSION

$ZnI_2$ based GPEs complexed with PMMA are suitable for ambient temperature applications. They are predominantly ionic conductors. They do not show very satisfactory performance when used for DSS cells. But, mixing them with a bulky cation salt, their performance can be improved very much. Further studies are being carried out to improve the performance by varying the composition of the salt mixture.

## ACKNOWLEDGEMENTS

Financial assistance received by Wayamba University of Sri Lanka under the research grant, SRHDC / RP / 04 / 13 / 01 and National Research Council of Sri Lanka under the research grant 12-109 are highly acknowledged.

## REFERENCES

1. Sokolsky, M. and Cirak, J., *Dye sensitized solar cells, materials and processes* Act. Electrotech et Info, 10/3, (2010) 78-81
2. O 'Regon, B. and Gratzel, M., *Low cost high efficiency solar cell based on dye sensitized colloidal $TiO_2$ films*, Nature, 353, (1991) 737-740
3. Paulsson, H., Kloo, L., Hagfeldt, A. and Boschloo, G., *Electron transport and recombination in dye sensitized solar cells with ionic liquid electrolytes*, J Electroanal Chem, 586, (2006) 56-61
4. Iqbal, H., Perera, K., Senevirathne, V.A., Rupasinghe, W.N.S., Thotawaththage, C.A., Senadheera, G.K.R. and Dissanayake, M.A.K.L., *Dye sensitized solar cells with polymethylmethacrylate based gel polymer electrolyte and tetrapropylammonium iodide salt*, Proc. Solar Asia Int Conf (2011) 163-168
5. Senevirathne, A.M.C., Senevirathne, V.A., Illeperuma, O.A., Bandara, H.M.N. and Rajapakse, R.M.G., *Fabrication of quasi solid state electrolyte for dye sensitized solar cells using fumed silica as the gelling agent*, Proc. Pera Uni Inter Res Sessions 18, (2014) 462
6. Dissanayake, M.A.K.L., Bandara, L.R.A.K., Bokalawela, R.S.P., Jayathilake, P.A.R.D. and Illeperuma, O.A., *A novel gel polymer electrolyte based on PAN and its application in a solar cell*, Mat Res Bul 37/5, (2002) 867-874
7. Yang, H., Huang, M. Wu, J., Lan, Z., Hao, S. and Lin, J., *The polymer gel, electrolytes based on PMMA and its application in quasi solid state dye sensitized solar cells*, Mat Chem and Phys, 110, (2008) 38-42

8. Thotawaththage, C.A., Senadeera, G.K.R., Bandara, T.M.W.J. and Dissanayake, M.A.K.L., *Mixed cation effect in enhancing the efficiency of dye sensitized solar cells based on PAN and nano porous $TiO_2$*, Proc. Solar Asia 2011 Int. Conf., Institute of Fundamental Studies, (2011) 175-179
9. Jayathilake, Y.M.C.D., Bandara, L.R.A.K., Vidanapathirana, K.P. and Perera, K.S., *Optimization of conductivity of the gel polymer electrolyte based on polymethylmethacrylate,* Proc. Inst of Phys Sri Lanka Tech Sess 20, (2014) 27-33
10. Arof, A.K., Aziz, M.F., Noor, M.M., Careem, M.A., Bandara, L.R.A.K., Thotawaththage, C.A., Rupasinghe, W.N.S. and Dissanayake, M.A.K.L., *Efficiency enhancement of mixed cation effect in dye sensitized solar cells with a PVDF based gel polymer electrolyte*, Inter Jour of Hydro Ener, 39, (2014) 2929-2935
11. Al Bat Hi, S.A.M., Alaei, I. and Sopyan, I., *Natural photosensitizers for dye sensitized solar cells*, Inter Jour of Renew Ener Res, 3/1, (2013) 138-143
12. Perera, H.A.C.S., Perera, K., Vidanapathirana, K., Senevirathne, V.A., Rupasinghe, W.N.S., Thotawaththage, C.A., Senadheera, G.K.R. and Dissanayake, M.A.K.L., *Quasi solid State dye sensitized solar cells with PVdF based gel polymer electrolyte and nano porous $TiO_2$ electrode*, Proc. Solar Asia 2011 Int. Conf., Institute of Fundamental Studies, (2011) 186-192