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MIXED CATION EFFECT ON THE PERFORMANCE OF DYE SENSITIZED SOLAR CELLS BASED ON PMMA GEL POLYMER ELECTROLYTE

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ABSTRACT

Gel polymer electrolyte (GPE)s have received a considerable attention to be used for dye sensitized solar cells(DSSC) as they do not exhibit the drawbacks of liquid electrolytes. It has been realized that cations in the salt of GPE play a great role in determining the efficiency of DSSC s. This paper reports about the effect of mixed cations on the performance of dye sensitized solar cells based on polymethylmetacrylate (PMMA) based gel polymer electrolyte. Two cations of dissimilar size were used for preparing the gel polymer electrolytes in the DSSCs. A mixture of zinc iodide (ZnI_2) with tetrapropylammonium iodide (Pr_4NI) was used in this regard. Conductivities of the GPES with only Pr_4NI and ZnI_2 alone exhibited values of $6.87\times10^{-3}Scm^{-1}$ and 5.62×10^{-3} Scm^{-1} respectively. But the mixed system showed a conductivity of 6.78×10^{-3} Scm^{-1}. Solar cells of configuration FTO/TiO_2/Dye/electrolyte/Pt/FTO were fabricated using a mesoporous Titanium dioxide (TiO_2) electrode sensitized with a Ruthenium dye. The cells with Pr_4NI and ZnI_2 alone gave efficiencies of 1.4% and 0.57% respectively. Mixed system showed an efficiency of 1.14%. This shows that lower efficiency of a DSSC fabricated with a salt like ZnI_2 can be improved using salt having a bulky cation.

Keywords: PMMA, Dye-sensitized solar cells, mixed cation effect, Gel polymer electrolytes.

1. INTRODUCTION

Dye sensitized solar cells (DSSCs) were introduced by Gratzel in 1991[1]. A typical DSSC consists of a photo-electrode with a dye-sensitized mesoporous Titanium dioxide (TiO_2) layer coated on an indium–tin oxide(ITO) glass and a liquid electrolyte containing an iodide/triiodideredox mediatori A platinum(Pt) metal is used as the counter electrode. Such DSSCs sensitized with ruthenium based dyes work well and show good efficiencies.

Some of the major problems with the liquid electrolyte based DSSCs is their poor long term stability due to evaporation, leakage and flammability of the liquids as well as decomposition of the dye. It has been understood that problems can be solved by using polymer based gel type electrolytes as they have reasonable ionic conductivities and mechanical flexibilities resulting satisfactory performances.

Iodide salts are used in most GPEs based DSSCs and hence the iodide ion conductivity in the electrolyte is major factor that determines the short circuit current density (J_{SC}) and also the efficiency of a DSSC[2]. Salts containing large cations such as tetrapropyl ammonium iodide (Pr_4NI), tetra-n-butyl ammonium iodide (Bu_4NI) and 1-Methyl-3-propylimidazolium iodide (IM3PII) are widely used as ionic salts to increase the iodide ion contribution. It is due to the fact that bulky cations in those salts are weak in mobility and therefore iodide ions are freed to move and they give rise to higher performance of DSSCs.

2. EXPERIMENTAL

2.1 Preparation of gel polymer electrolyte

Polymethylmetacrylate(PMMA, ALDRICH), Ethylene Carbonate (EC, ALDRICH), Propylene Carbonate (PC, ALDRICH), Tetra Propyl Ammonium Iodide (Pr_4NI, ABCR), Zinc Iodide (ZnI_2, ALDRICH) were used as received. Iodide (I_2, Breckland Scientific Suppliers) was also used without any treatment.

The electrolyte samples were prepared by keeping the weights of PMMA (0.02g), EC(0.03g) and PC(0.03g) unchanged and changing the individual weights of Pr_4NI and ZnI_2 so that their total weight remain at 0.04g. The weight of iodine (I_2) was taken to be 3% of the total mole amount of salts.

Then, the required amounts of PMMA, EC, PC, ZnI_2 and Pr_4NI were weighed and the mixture was stirred magnetically while heating at 60 ^{0}C for a time period of one hour. After that I_2 was added. Then, the hot viscous mixture was pressed in between two well cleaned glass plates and put in the vacuum desiccator overnight. It was possible to get a stable film free from holes. All the samples were prepared changing amounts of ZnI_2 and Pr_4NI.

2.2 AC impedance measurements

The ionic conductivities of the gel polymer electrolyte samples were determined by the computer controlled MetrohmAutolab Impedance Analyzer M101 in the frequency range of 20Hz-10Hz. Disc shaped electrolyte samples were loaded between two polished stainless steel electrodes inside a sample holder. Impedance measurements were taken at room temperature.

2.3 DC Polarization test

The GPE was put in to the sample holder. Then current through the GPE film was measured as a function of time by applying 1 V potential to the GPE film. DC polarization gives the nature of ionic conductivity corresponding to the compositions. Ionic transference was measured using following equation.

Ionic Transference (T_{ion}) = $(I_T - I_E)/I_T$

2.4 Fabrication of DSS cells

First Fluorine doped Tin Oxide (FTO) glass strips (5mm*20mm) were cleaned using standard method and boiled in propone-2-ol.

Titanium dioxide (TiO_2, Degussa) was weighted and grinded for about one minute without adding anything. Then 3 drops of acetic acid were added and grinding was done for few minutes. After that 1 drop of Triton X and 3 drops of acetic were added and mixture was grinded until it became a pulp. Then 6 drops of acetic acid and few drops of ethanol were added into the mixture and grinding was continued until all TiO_2 particles were grinded well. Ethanol amount in the mixture were kept in a certain limit by adding few drops time to time while grinding.

After preparing the paste, electrodes were prepared by blading it on FTO glass strip and those glasses were kept to dry in open air. When paste was completely dried, (5mm*5mm) area was created by scratching off excess TiO_2 paste. Finally above electrodes were sintered at 450^0C for 45 minutes. Sintered electrodes were dipped in Ruthenium dye for 24 hours before use for solar cells.

Solar cell was prepared by sandwiching electrolyte in between two electrodes in configuration FTO-TiO_2-Dye-Gel polymer electrolyte-Pt-FTO. Above procedure was repeated for following GPE compositions.

- PMMA,EC,PC and Pr_4NI
- PMMA,EC,PC and ZnI_2
- PMMA,EC,PC, ZnI_2 and Pr_4NI

2.5 Characterization of DSS cells

Photo current – voltage curves were obtained for three cells under the illumination of 100W.

3. RESULTS AND DISCUSSION

3.1 Characterization of the gel polymer electrolyte

The compositions of the PMMA based gel polymer electrolyte, containing I_2 and different percentages of the binary iodide mixture $Pr_4N^+I^-$ and ZnI_2, PMMA: EC: PC. The conductivity variation with temperature for different electrolyte compositions are shown in Figure 1 in the form conductivity (on log scale) plotted against the reciprocal temperature. The electrolyte containing only ZnI_2 as the salt has the lowest conductivity at all measured temperatures. This electrolyte has a conductivity of $5.62\times10^{-3}Scm^{-1}$. The electrolyte containing only Pr_4NI shows the highest conductivity of $6.87\times10^{-3}Scm^{-1}$.

Table 1: Room Temperature conductivity

Composition	Room Temperature conductivity (1×10^{-3} Scm^{-1})
Pr_4NI	6.87
ZnI_2	5.62
$Pr_4NI + ZnI_2$	6.78

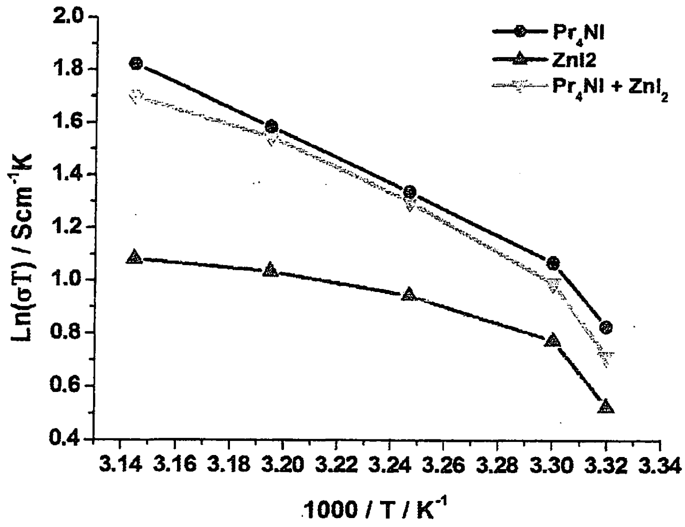
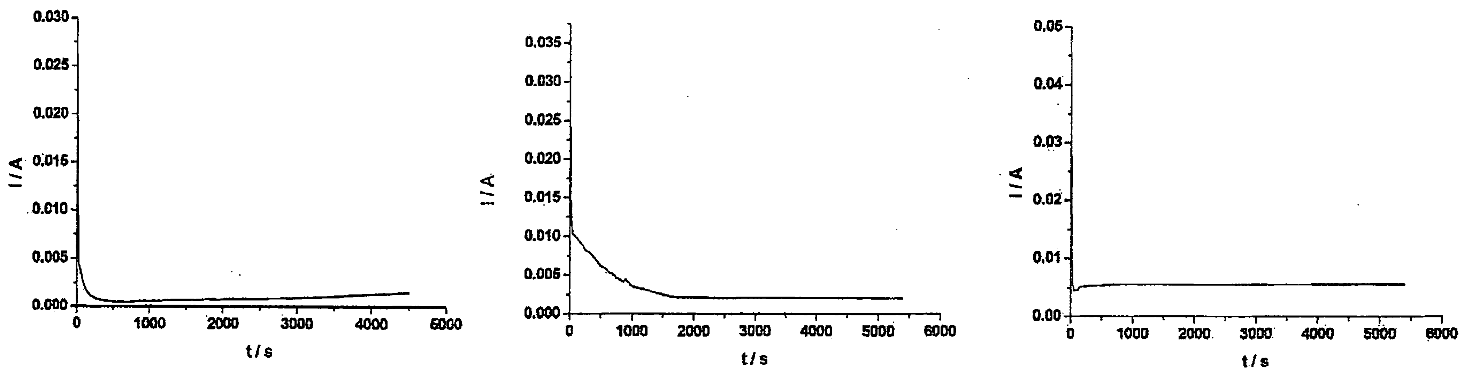


Figure 1: the variation of ionic conductivity vs. temperature

The ionic conductivity of the gel type electrolyte results mainly from movement of ions dissociated in the "trapped" EC/PC co-solvent in the PMMA polymer matrix.

3.2 DC Polarization test



2a 2b 2c

Figure 2: DC Polarization

According to the above graphs and corresponding to current variation with time for the cell configuration stainless steel (SS) Electrode / Gel Polymer electrolyte / stainless steel (SS) electrode 2a – Pr_4NI system t_{ion} = 0.98 2b - ZnI_2 system t_{ion} = 0.93 2c – Mixed system t_{ion} = 0.92.

3.3 Characterization of DSSC

Under the irradiation of 100 W, the open circuit voltage (V_{oc}) and the short circuit current density (J_{sc}) were measured. In addition, the fill factor (FF,%) and efficiency (η%) were calculated for all the cells studied. The fill factor was calculated using

$$FF = J_{opt} V_{opt} / J_{sc} V_{oc}$$

Where J_{opt} and V_{opt} are the current density and voltage respectively at maximum power output.

η was calculated using

$$\eta = J_{sc} V_{oc}\, FF / \text{Total incident power density}$$

Table 2: parameters of solar cells

compositions / Parameters	Pr_4NI	ZnI_2	$Pr_4NI + ZnI_2$
Voc(mV)	438	246	425
JM(μAcm-2)	14.4	11.2	12.4
Isc (μA)	7.1	2.8	5.2
Jsc(μAcm-2)	28.4	11.2	20.8
Fill factor (%)	36	66	41
Efficiency (%)	1.4	0.57	1.14

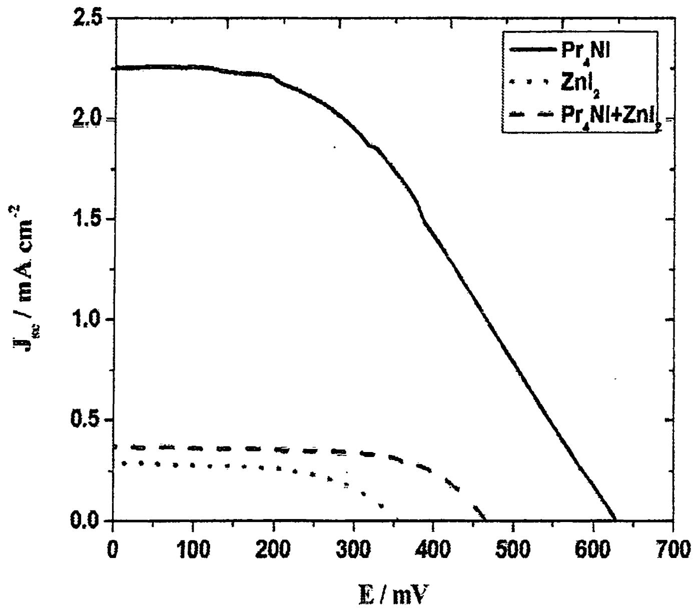


Figure 3: I-V curves

Table 2 shows the parameters of solar cells with three different electrolytes and figure 3 shows the current-voltage characteristics of the three different types of solar cell. Considering three compositions, highest V_{oc} value can be seen at the Pr_4NI system. Although ZnI_2 system has the lowest V_{oc}. But V_{oc} value can be increased by mixing ZnI_2 with Pr_4NI. It may be due to the mixed cation effect. Also Pr_4NI system has obtained the maximum efficiency than the other two systems.

4. CONCLUTION

Polymer gel electrolytes were synthesized by hot press method taking poly (methyl methacrylate) (PMMA) as polymer, (EC + PC) ethylene carbonate +propylene carbonate as solvents and polymethylmetacrylate (Pr_4NI) and zinc iodide (ZnI_2) as salt. Different samples were prepared by taking alone Pr_4NI, ZnI_2 and $Pr_4NI + ZnI_2$.

The dye-sensitized solar cells fabricated with PMMA based polymer electrolytes with a binary iodide salt system consisting of a small alkali cation (Zn^+) and a bulky cation (Pr_4N^+) show efficiency enhancement which can be attributed to the mixed cation effect.

It should be noted that current density and efficiency of gel based DSSCs are not determined by the total lionic conductivity of the electrolyte but by many factors. In fact the net result of several competing factors in the electrolyte determines the net short circuit current density and hence the efficiency such asthe number of free I-ions and their mobility, the number Zn^{+} ions and their mobility, the number of Pr_4N^{+} ions and their mobility, the number of ion aggregates and the viscosity ofthe electrolyte solution. The combination of this entire rise to the maximum efficiency with the 1.14%.

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