

## VARIATION OF IONIC CONDUCTIVITY AND SOLAR CELL CHARACTERISTICS OF A GEL POLYMER ELECTROLYTE BASED ON DIFFERENT IODIDE SALTS

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### ABSTRACT

Solar power has a great potential as a source of renewable energy due to decrease of fossil supply. Solar cell is a device that directly converts light energy into electrical energy through the photovoltaic process. The performance and effectiveness of a solar cell device mainly depend upon its design and the properties of the photo voltaic materials. In this study, gel polymer electrolyte (GPE) based on polyvinylidene fluoride (PVdF), ethylene carbonate (EC) and propylene carbonate (PC) has been investigated to be used for solar cells. GPE was prepared by using different iodide salts RI ( $R^+ = Pr_4N^+, K^+, Mg^{2+}, Zn^{2+}, Na^+$ ) using hot pressed method. The effect of  $R^+$  in GPE on the variation of the ionic conductivity and the performance of dye sensitized solar cells (DSSCs) were studied in this investigation. The composition, 100 polyvinylidene fluoride (PVdF) / 400 ethylene carbonate (EC) / 400 propylene carbonate (PC) / 100 Tetrapropylammonium iodide, ( $Pr_4N^+I^-$ ) showed the conductivity of  $3.73 \times 10^{-3} \text{ Scm}^{-1}$  at  $28^\circ\text{C}$ . The cell in the form glass/ FTO/  $TiO_2$ / Dye/ GPE/ Pt/ FTO/ glass showed an average open circuit voltage of 693 mV. The average short circuit current was 3.1 mA.

**Keywords:** Gel polymer electrolyte; Hot pressed method; Polyvinylidene fluoride; Tetrapropylammonium iodide

### 1. INTRODUCTION

During the past decades, there was a lot of effort done on developing gel polymer (GPEs) electrolytes to compete with liquid counterparts. GPE has a solid like cohesive property and liquid like diffusive property. They are generally prepared by adding a polymer to a liquid electrolyte. A salt is dissolved in polar solvent/s to prepare a liquid electrolyte. Ethylene

carbonate (EC), propylene carbonate (PC), diethyl form amide (DMF), diethyl carbonate (DEC), diethyl carbonate (DMC) etc. are generally used as solvents. Solvents are usually of low molecular weight which increases the conductivity by providing a locally mobile coordination environment for ion motion<sup>5</sup>. The salt provides ion for conduction and it should have low activation energy. The macro-molecular polymer provides the mechanical strength to the system. Polymers like poly (acrylonitrile) (PAN), poly (methyl methacrylate) (PMMA), poly (vinylidene fluoride) (PVDF) etc. are generally used for preparation of GPEs.  
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Polymer gel electrolytes have high ionic conductivities as required for device application such as lithium batteries, super-capacitors and electrochemical devices. Another interesting and emerging area for possible applications is in the dye sensitized solar cells (DSSCs). The major drawback of DSSCs using liquid electrolytes is the less long-term stability due to the volatility of the electrolyte.<sup>2</sup> Other than that, safety issues and less design flexibilities have been considered as some crucial issues for the use of liquid electrolytes in DSSCs. To overcome those problems, GPEs are being investigated to substitute the liquid electrolytes as they exhibit good ionic conductivities while maintaining solid state nature.<sup>3</sup>

In this work, the variation of ionic conductivity and the cell performance of DSSCs with GPEs prepared using different iodide salts RI ( $R^+ = Pr_4N^+I, K^+, Mg^{2+}, Zn^{2+}, Na^+$ ) were investigated.

## 2. EXPERIMENTAL

### 2.1 Preparation of GPE

Materials polyvinylidene fluoride (PVdF, ALDRICH), ethylene carbonate (EC, ALDRICH) and propylene carbonate (PC, ALDRICH) were used as received. For the purpose of measuring variation of the conductivity due to different iodide salts several GPE films were prepared by adding constant quantity of different iodide salts RI ( $R^+ = Pr_4N^+I, K^+, Mg^{2+}, Zn^{2+}, Na^+$ ) to the composition. The mixture was stirred magnetically at 100 °C for 30 min until the entire salt has been dissolved. Required amount of PVdF was added to the above mixture and heated up to 120 °C and kept for 15 min while stirring for PVdF to fully dissolve and then iodine was added. The weight of iodine was taken to be one tenth of the total mole amount of the iodide salts. Finally, the homogeneous, hot mixture was pressed in between two well cleaned glass plates. Samples were prepared by varying the RI.<sup>1,4</sup>

## 2.2 AC impedance measurements

A circular shape sample of 14 mm diameter was cut from a prepared GPE film and was sandwiched in between two stainless steel (SS) electrodes in a spring loaded sample holder. Impedance data were gathered in the frequency range, 100 kHz – 0.01 Hz from room temperature to 50 °C using Metrohm Autolab Impedance analyzer.

## 2.3. DC polarization measurements

A circular shape sample was loaded in between two platinum (Pt) electrodes and current drop with time was measured for 2 hours under a dc potential of 1 V.

## 2.4. Photo electrode preparation

Fluorine-doped conducting tin oxide (FTO) strips were cleaned and boiled in Propone-2-ol. 3 drops of Acetic acid and 1 drop of Triton x were added and mixture was grinded until it become a pulp. Ethanol amount in the mixture were kept in a certain limit by adding few drops time to time while grinding. Electrodes were prepared by doctor blade method FTO glass strips and those glasses were kept to dry in open air and 10mm\*10mm area was created by scratching off excess TiO<sub>2</sub> paste. Electrodes were sintered at 450 °C temperature for 45 minutes and dipped in Ruthenium dye for 24 hours.<sup>2, 5</sup>

## 2.5. DSSC fabrication and characterization

Three samples were selected for cell fabrication. The DSSCs having the configuration glass/ FTO/ TiO<sub>2</sub>/ Dye/ GPE/ Pt/ FTO/ glass were fabricated by sandwiching the gel polymer electrolyte in between the dye sensitized TiO<sub>2</sub> electrode and a Pt glass. Open circuit voltages and short circuit currents were measured using a digital multimeter. Charging discharging characteristics were observed under the illumination of 100 W.

## 3. RESULTS AND DISCUSSION

Table 1: Conductivity of different salts at room temperature

Sample	Conductivity at room temperature (28 °C ) (10 <sup>-3</sup> Scm <sup>-1</sup> )
KI	12.0
Pr <sub>4</sub> NI	3.73
ZnI <sub>2</sub>	2.44
NaI	2.68
MgI <sub>2</sub>	1.17

### 3.1. Ionic conductivity of GPEs

Three samples that result high room temperature conductivities which are selected based on 1<sup>st</sup> and the 2<sup>nd</sup> group of the periodic table are shown in Figure 1 (a).

There are two very clear features in the figure and they are,

I. Conductivity increases with increasing temperature.

When temperature increases, viscosity goes down resulting conductivity increment. Also some researchers have disclosed these phenomena as due to hopping mechanism between coordinating sites, local structural relaxations and segmental motion of polymer. <sup>2</sup>

II. Conductivity temperature behavior can be explained by Vogel – Tamman – Fulcher (VTF) equation.

When conductivity is correlated by VTF, it is said to be depending on free volume theory. That is, the mobility of charge carriers is governed by polymer segmental motion by providing sufficient free space. As per the observation in Figure 1 (a) it can be suggested that polymer segmental motion imparts a considerable effect on conductivity of the GPE. In literature there are some reports about GPEs that have shown Arrhenius behavior instead of VTF. <sup>3, 6</sup>

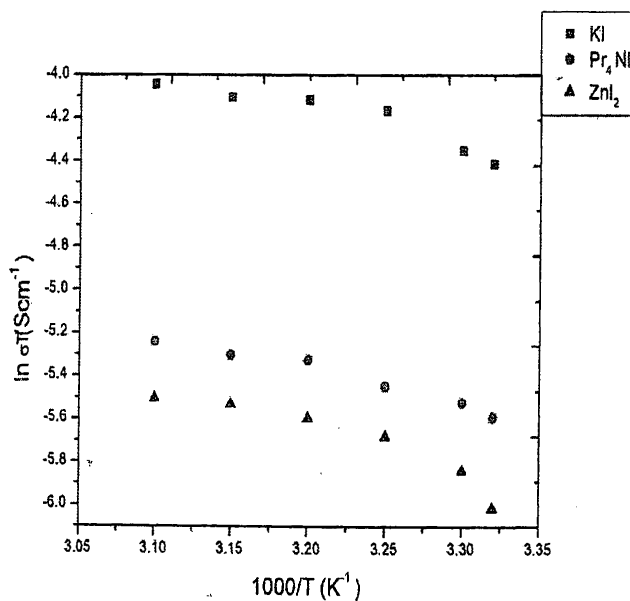


Figure 1 (a): Variation of conductivity with inverse temperature

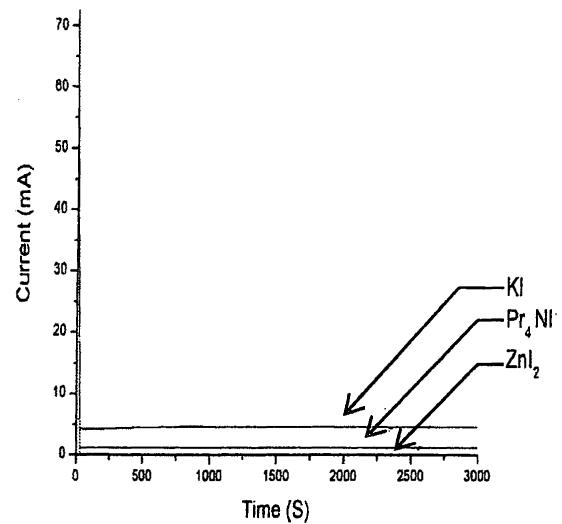


Figure 1(b): DC polarization curve taken with blocking electrodes

### 3.2. DC polarization test

Since the electrodes are blocking ions, Figure 1 (b), the sudden drop of current is due to ions and the steady state constant current is due to electrons. Ionic transference number  $t_{ion}$  was calculated as;  $(t_{ion}) = (I_T - I_E)/I_T$  <sup>5</sup>

The value of  $t_{ion}$  has been calculated and found to be 0.9. This value clearly shows that overall conductivity of GPE is pure ionic. <sup>3</sup>

### 3.3. Solar cell characterization

Even though conductivity of KI is higher than  $Pr_4N^+I^-$ , overall cell efficiency of  $Pr_4N^+I^-$  is higher than KI. When the cation of the salt is larger, it becomes less mobile. Due to this, anion movement increases and hence, anion contribution for cell performance improves. <sup>5,6</sup>

Table 2: System comparison for the solar cells for the selected three samples

	System 1		
	KI	$Pr_4NI$	$ZnI_2$
$V_{oc}(*10^{-3})$ V	661.2	693	593.8
$I_{sc}(*10^{-3})$ A	2.08	3.1	1.68
FF	0.367	0.473	0.489
$\eta$	82,873	162,345	80,224

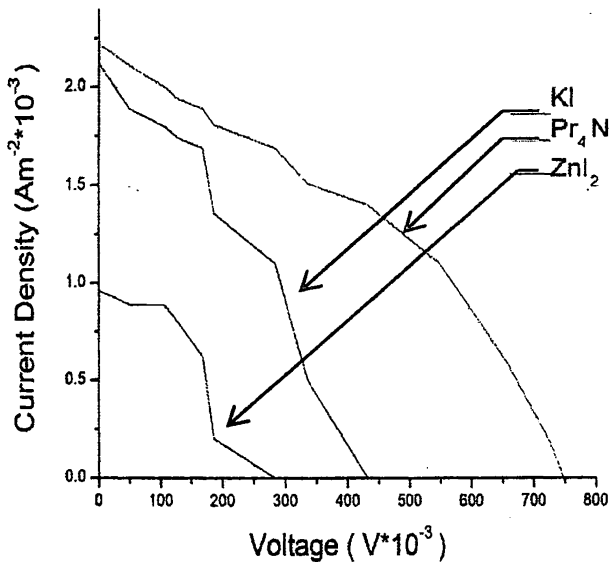


Figure 2 (a): IV Characteristic curves for the DSSC of the configuration FTO/TiO<sub>2</sub>/ Dye/ GPE/ Pt/ FTO.

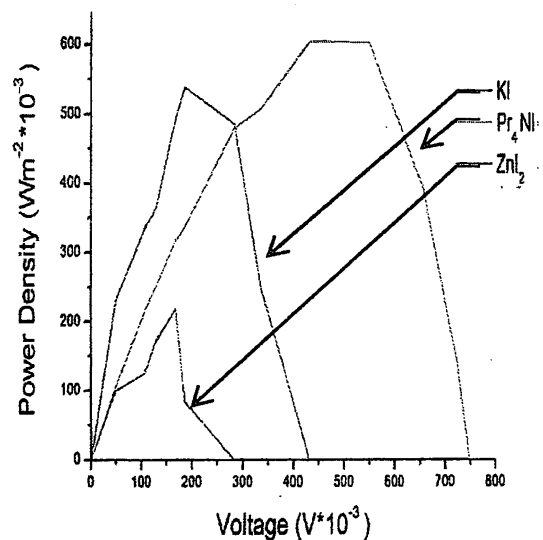


Figure 2 (b) PV Characteristic curves for the DSSC of the configuration FTO/TiO<sub>2</sub>/ Dye/ GPE/ Pt/ FTO.

#### 4. CONCLUSION

Among the GPEs studied, the system with KI shows the highest conductivity. But Pr<sub>4</sub>NI based GPE which has the second highest conductivity shows the best solar cell performance. This elucidates the fact that conductivity and the solar cell performance are not directly related to each other. Due to mono valency of K and I, system based on KI can show higher conductivity. In Pr<sub>4</sub>NI though Pr<sub>4</sub>N<sup>+</sup> and I<sup>-</sup> are mono valent ions, due to bulky size of Pr<sub>4</sub>N<sup>+</sup>, conductivity of the system may be lower. But due to same reason, I<sup>-</sup> contribution for the cell performance increase in the later system.

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