



Influence of Succinonitrile and Potassium Iodide Concentration on Ionic Conductivity and Performance of Dye-Sensitized Solar Cells Based PMMA-PVA Polymer Blend Electrolyte

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Polymer blend electrolytes based on PMMA (80 %)/PVA (20 %) with distinctive weight ratio of potassium iodide and succinonitrile using dimethyl sulfoxide as solvent have been used to prepare gel electrolytes using solution cast technique. The ionic conductivity values increase with increasing succinonitrile weight ratio up to 5 % beyond which the conductivity values decrease and the highest ambient temperature conductivity has been found to be 3.7×10^{-3} S/cm. At high concentration of succinonitrile (more than 5 wt. %) leads to a decrease in the value of the ionic conductivity due to the less number of available charge carriers. The conductivity for each gel polymer electrolyte has increased with increasing temperature range from 298 to 373 K. This is evidently due to the increase in ion mobility and the decrease of viscosity with increasing temperature. Dye-sensitized solar cells with 30 % wt. KI as the only iodide salt shows efficiency 3.75 %, whereas dye-sensitized solar cells utilizing 25 % KI: 5 % succinonitrile weight ratio shows efficiency 4.28 %, under AM 1.5 (1000 W m⁻²) illumination.

Keywords: Gel polymer electrolyte, Succinonitrile, Potassium iodide, Dye-sensitized solar.

INTRODUCTION

In the late years, there has been an enormous interest in the preparation of polymer electrolytes with high ionic conductivity, good mechanical strength and thermal stabilities [1] as these polymer electrolytes assume a noteworthy part in solid state batteries, electrochromic devices, chemical sensors, fuel cells, super capacitors *etc.* [2,3]. Ionic conductivity is the main aspect in the polymer electrolytes, which is closely related to the viscosity. Low viscosity of sample will produce higher ionic conductivity by forming more voids within the polymer matrix [4]. Polymer gel electrolytes (PGEs), a potential alternative to liquid and solid electrolytes, have high ionic conductivity and good stability, due to the polymer matrix which can effectively trap the liquid solvent to inhibit evaporation and provide channels for fast transport of redox couples. Poly(vinyl chloride) (PVA) has strong adhesion and good solubility in polar solvents. These properties may enhance the interfacial contact between the polymer gel electrolyte and photoanodes [5]. The improved power conversion efficiency of solar cell is based on the ionic conductivity of polymer electrolytes. Dye-sensitized solar cells (DSSCs) have attracted great attention in the widespread research community as a clean, low cost technology and high power conversion efficiency. Typical dye-

sensitized solar cells consist of dye-sensitized nanocrystalline TiO₂-layer-coated fluorine-doped tin oxide (FTO) photoanode, iodide/triiodide redox electrolyte and platinum coated FTO photocathode. Both electrolyte and dye play an important role for obtaining high power conversion efficiency and long-term stability of DSSCs [6,7]. Succinonitrile, a plastic crystal between -35 (crystal to plastic crystal phase transition temperature, T_{pc}) and 54 °C (melting temperature, T_m), has had immense widespread interest in recent years. Succinonitrile (Succ) is a low molecular weight, low melting temperature, waxy nature, economically low-cost and high dielectric constant plastic crystal. It offers high molecular diffusivity and plasticizing properties [8,9]. In the present paper, we report the plasticizing effect of K⁺ ions and succinonitrile on the ionic conductivity of a new redox-couple gel polymer electrolyte system, PMMA-PVA. Potassium iodide was used as an ionic salt as K⁺ ion assists in separating the polymeric chains and thus acts as a plasticizer. A current *versus* voltage study of DSSC prepared using the (80 % PMMA: 20 % PVA) blend KI/Succ-I₂ electrolyte, is reported.

EXPERIMENTAL

Electrolyte preparation: PMMA with an average molecular weight of 996,000 and PVA, 99 % hydrolyzed with

molecular weight of 130000 g mol⁻¹). Dimethyl sulfoxide (DMSO) used as solvent, succinonitrile (Succ, 99 %) and KI, all above purchased from Sigma Aldrich. Iodine chips were obtained from Fluka Switzerland. All the materials were used as received. Fixed amount of PMMA-PVA, 80 %/20 % weight ratio was used. Electrolytes with six different compositions were prepared using solution cast method by varying the weight ratio of KI and succinonitrile, to be 30:0, 28:02, 25:05, 23:07, 20:10 and 18:12 as shown in Table-1. Appropriate amounts of PMMA-PVA, KI and succinonitrile were dissolved in DMSO. The mixtures were stirred at 110 °C for 1 h until gel polymers are formed. When the gel is formed, the heater was immediately stopped and the gel was allowed to cool down. On reaching room temperature I₂ (10 mol % of KI/Succ) was added into the gel electrolyte. The homogenous gel polymer electrolyte was placed in desiccators overnight before being used in dye-sensitized solar cells.

TABLE-1
ASSIGNING AND COMPOSITION OF
PMMA-PVA-KI/Succ GEL ELECTROLYTES SYSTEM

Assigning	PMMA (%)	PVA (%)	KI (%)	Succ (%)
M0	80	20	0	0
M1	80	20	30	0
M2	80	20	28	2
M3	80	20	25	5
M4	80	20	23	7
M5	80	20	20	10
M6	80	20	18	12

Electrical impedance spectroscopy measurement:

HIOKI 3532-50 LCR Hi-Tester has been used to measure the impedance of the electrolytes in the frequency range 50 Hz to 5 MHz. The samples were sandwiched between two stainless steel disc electrodes and the impedance measurements were carried out at different temperatures ranging from 298 to 373 K. The bulk resistance R_b of each sample was determined from the intercept of the Nyquist plot with the real impedance axis. The ionic conductivity, σ of the sample was calculated using the eqn. 1:

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where, t is the thickness of the sample, R_b is the bulk resistance obtained from the complex impedance plot and A is the film-electrode contact area.

Dye-sensitized solar cell fabrication and J-V characteristics:

Dye-sensitized solar cells were fabricated by sandwiching gel polymer electrolytes (GPEs) between TiO₂/dye electrode and platinum counter electrode in the configuration of FTO/TiO₂/Dye/GPE/Pt/FTO. TiO₂ functions as the base material for the photoanode and has the ability to form a large network for electron flow, good transparency and a large energy band gap of 3 to 3.2 eV [4]. TiO₂ paste for the photoanode was prepared by grinding 0.2 g of nano TiO₂ powder (Degussa P25) in a mixture of 2 mL ethanol, 12 drops of glacial acetic acid and 1 drop of surfactant (Triton X-100). The TiO₂ paste was spread on fluorine-doped tin oxide (FTO) glasses using the doctor-blade method to have 5-10 μm film thickness and sintered at 450 °C for 45 min. The TiO₂ electrode was then

immersed in a ruthenium 535 (N3) dye solution diluted with ethanol to 5 mill mol for 24 h for dye adsorption. The TiO₂/dye electrode was then washed with acetone to remove the unbound TiO₂ particle and unadsorbed dye. A Keithley 2400 source meter was used to measure the photocurrent density-voltage (J-V) characteristics of the DSSCs at room temperature (298 K) under 1000 W m⁻² illumination. From the J-V plots, the current density, J_{opt} and voltage, V_{opt} at maximum power output were obtained and used in the eqn. 2 to calculate the fill factor (FF):

$$\text{Fill factor (FF)} = \frac{J_{opt} V_{opt}}{J_{sc} V_{oc}} \quad (2)$$

In eqn. 2, J_{sc} is the short circuit current density and V_{oc} is the open-circuit voltage. The FF value was then used to calculate the overall energy conversion efficiency, η of the cell using the eqn. 3:

$$\eta (\%) = \frac{J_{sc} V_{oc} FF}{P_{in}} \times 100 \quad (3)$$

P_{in} in eqn. 3 is the total incident power density.

RESULTS AND DISCUSSION

Ionic conductivity of gel polymer electrolytes: Ionic conductivity plays a predominant role to produce better polymer electrolytes leading to battery applications. The ionic conductivity in polymer electrolytes is assumed to occur by Lewis acid-base interaction between cation and polymer [10,11]. The electrochemical impedance spectroscopy is an excellent tool to characterize many of the electrical properties of the material and their interfaces with the electrode materials. In the present study the ionic conductivities of PMMA-PVA gel polymer electrolyte with different concentration of KI and succinonitrile, have been analyzed. Fig. 1 shows the variation of ionic conductivity of the electrolytes with different weight ratio of KI and succinonitrile at temperatures ranging from 298 to 373 K. The resulting conductivity is mainly due to the overall mobility of ions and polymer segment, which is determined by the free volume and this leads to the increase in ionic conductivity and segmental mobility. This assists ion transport and compensates the retarding effect of the ionic clouds [12]. At low salt concentrations, ionic conductivity was lower but with increasing concentration, ionic conductivity increased. After a certain salt concentration, further addition of salt reduced conductivity. Several other researchers have observed similar feature and have reported that the initial conductivity increase may be due to the building up of charge carriers with increasing salt content [13,14]. At high salt concentrations, buildup of charge carriers is offset by the formation of neutral ion pairs as well as ion clouds made up of ion aggregates. The sample that had the optimized mechanical stability and highest ionic conductivity was of the composition, 20 PMMA/30 EC/30 PC/40 Pr₄N⁺I⁻ (in weight basis) and the conductivity was 5.02×10^{-3} S cm⁻¹ at 28 °C. This value is rather higher than the values reported by Jeong *et al.* [15] for a polyvinyl alcohol based MgTF system. Fig. 1 showed that when the temperature increases, the conductivity also increases as expected. This is evidently due to decrease of viscosity with increasing temperature.

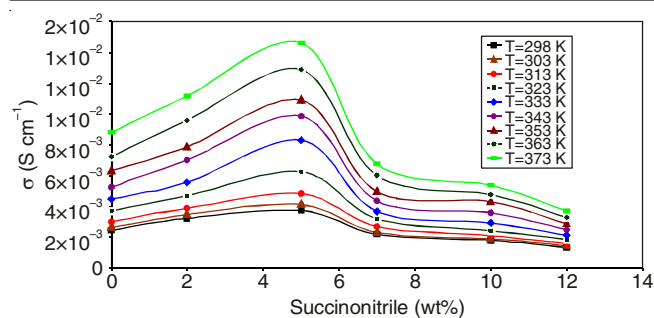


Fig. 1. Ionic conductivity of PMMA-PVA-KI/Succ, gel electrolytes system at various temperatures

It is clear from Fig. 1, as the temperature increases, the conductivity increases for all the complexes irrespective of salt concentration this due to internal activation and the reduce of the crystalline nature of the polymer-salt complexes. The plots suggest that the non-linear ion transport in polymer electrolyte depends upon the segmental motion of the polymer electrolyte [1]. The rising temperature increases the vibrational energy of the polymer segment, enabling it to push against the hydrostatic pressure imposed by its neighboring atoms and creating a small amount of space surrounding its own volume through which the ionic motion can occur. Furthermore due to the increase in volume, it reduces the retarding effect of ion clouds, which could be the reason for higher conductivity at elevated temperatures. Arrhenius plot of the ionic conductivity for PMMA: PVA blend with different salt weight ratio is shown in Fig. 2.

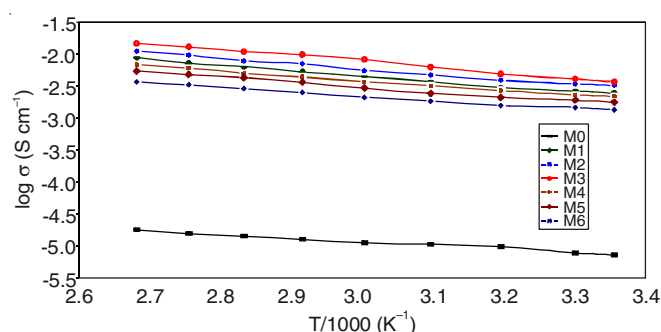


Fig. 2. Temperature dependence of the ionic conductivity of the samples

The amorphous nature of the present polymer electrolyte facilitates the fast K^+ ion motion in the polymer network and it further provides a higher free volume on increasing the temperature. The polymer electrolyte consists of 25 % KI/5 % succinonitrile, has high ionic conductivity of 3.7×10^{-3} S/cm at room temperature. Beyond this concentration ionic conductivity decreases. This is due to the formation of ion pairs and the ion triplets, which causes constraints in the polymer segmental motion and also retards the ionic mobility due to the increase in crystalline nature of polymer electrolyte [3]. Besides that, the anions that interact with the polymer may also contribute to the ionic conductivity [7]. In supplement, the interaction between the polymer blend and nitrogen of succinonitrile, may result in a competition between polymer blend and nitrogen to bind K^+ ions, yielding more free ions for conduction. Thus, one can expect an improvement in the mobility and concentration of charge carriers due to high molecular diffusivity and plasticizing property of the succinonitrile

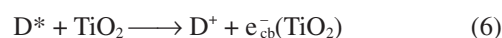
[8]. The addition of plasticizer initially leads to the formation of K^+ -Succ, complex (due to the high solvating power of succinonitrile) which reduces the formation of (PMMA/PVA)- K^+ -complex and increases the flexibility of the polymer chain. The ionic conductivity enhancement can be attributed to the decrease in crystallinity of PMMA/PVA, as well as the high polarity of succinonitrile, *i.e.*, its capability to act as a solvent for KI salt [9]. As succinonitrile is a non-ionic plastic crystal, the possibility of PMMA/PVA- K^+ -complex formation is more when its concentration is low, which leads to the increase in ionic conductivity. The high concentration of succinonitrile (more than 5 wt. %) leads to a decrease in the value of the ionic conductivity due to the less number of available charge carriers; the unreacted amount of succinonitrile could also act as an insulator, blocking ion motion in the membrane [10,16]. This means that at high succinonitrile content, ion aggregation occurs at a faster rate than ion dissociation in KI [17]. When the concentration of the filler is increased beyond 10 wt. % (not reported here), the ionic conductivity decreases due to phase discontinuities and dilution effect in the polymer system. These results are in accordance with the result of Scrosati *et al.* [13] using nano- Al_2O_3 as filler.

The working principal of DSSC can be summarized as follows:

Electrolyte [16]:



Photoanode:



Counter electrode:



where D represents the dye molecule and $h\nu$ is the light energy. The redox mediator concentration in the gel polymer electrolyte plays an important role in DSSC as shown in eqns. 4, 7 and 8. The redox mediator concentration can be increased by increasing the iodide salt content in the electrolyte [18]. Fig. 3 shows the photocurrent density-voltage (J-V) curves for DSSCs fabricated prepared with PMMA-PVA electrolytes having six different compositions of KI and succinonitrile at room temperature.

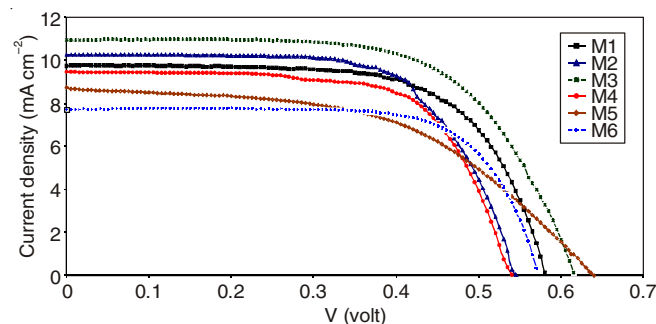


Fig. 3. J-V curves for DSSCs with different KI-Succ, gel electrolyte system

Table-2 lists the performance parameters for the DSSCs obtained from J-V curve analysis. Table-2, shows that the

TABLE-2
DSSC PARAMETERS WITH DIFFERENT KI/Succ GPE

Electrolyte	KI (%)	Succ (%)	J_{sc} (Ma/cm ²)	V_{oc} (volt)	FF	η (%)
M1	30	0	9.746	0.580	0.663	3.75
M2	28	2	10.260	0.545	0.667	3.73
M3	25	5	10.960	0.615	0.635	4.28
M4	23	7	9.460	0.540	0.668	3.41
M5	20	10	7.730	0.570	0.710	3.13
M6	18	12	8.740	0.640	0.510	2.85

efficiency of DSSCs increases as succinonitrile concentration increases from 0 up to 5 wt. %, than the efficiency decreases as succinonitrile concentration is increased beyond 5 wt. %. It is noted that the 25 % KI: 5 % succinonitrile based electrolyte resulted in a η of 4.28 %, which is nearly higher than that obtained for electrolyte with 30 % KI only (η 3.75 %). This suggests that the improved mobility and concentration of the charge carriers for the 80 % PMMA:20 % PVA blend-25 % KI/5 % Succ-I₂ due to high molecular diffusivity and plasticizing properties of succinonitrile which helped to improve the interfacial reactions between the dye-sensitized TiO₂ [19,20], electrolyte and platinum as evinced by the increased values of J_{sc} and fill factor. These studies indicate that high molecular diffusivity and plasticizing property of the succinonitrile played a vital role in improving the cell efficiency [21].

Conclusion

The plasticizing property of the succinonitrile played a crucial role to improve the ionic conductivity. The dependence of conductivity of polymer gel electrolytes on temperature was measured and a maximum room temperature (298 K). The incorporation of different compositions of plasticizer in the polymer matrix significantly enhanced the amorphous nature resulted in increase in ionic conductivity of polymer gel electrolytes. It resulted in a better interfacial contact between the electrolyte and dye-sensitized TiO₂ at the nonporous and finally improve photovoltaic property relative to those prepared using the PMMA/PVA- KI/Succ-I₂ based electrolyte.

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