

Research Article

Phthaloylchitosan-Based Gel Polymer Electrolytes for Efficient Dye-Sensitized Solar Cells

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Phthaloylchitosan-based gel polymer electrolytes were prepared with tetrapropylammonium iodide, Pr₄NI, as the salt and optimized for conductivity. The electrolyte with the composition of 15.7 wt.% phthaloylchitosan, 31.7 wt.% ethylene carbonate (EC), 3.17 wt.% propylene carbonate (PC), 19.0 wt.% of Pr₄NI, and 1.9 wt.% iodine exhibits the highest room temperature ionic conductivity of $5.27 \times 10^{-3} \text{ S cm}^{-1}$. The dye-sensitized solar cell (DSSC) fabricated with this electrolyte exhibits an efficiency of 3.5% with J_{SC} of 7.38 mA cm^{-2} , V_{OC} of 0.72 V, and fill factor of 0.66. When various amounts of lithium iodide (LiI) were added to the optimized gel electrolyte, the overall conductivity is observed to decrease. However, the efficiency of the DSSC increases to a maximum value of 3.71% when salt ratio of Pr₄NI : LiI is 2 : 1. This cell has J_{SC} , V_{OC} and fill factor of 7.25 mA cm^{-2} , 0.77 V and 0.67, respectively.

1. Introduction

A solar cell is a device that directly converts light energy into electrical energy through the photovoltaic process. The solar cells currently produced are generally divided into several types according to their material composition and operating mechanism, such as photoelectrochemical solar cells and thin film junction devices. Photoelectrochemical solar cells have become attractive devices since Gratzel and O' Regan first reported the prototype dye-sensitized solar cell (DSSC) using wide band gap TiO₂ semiconductor in 1991 [1]. The DSSC has gained a great deal of attention due to its relatively high energy conversion efficiency and low production cost [2]. DSSCs are also semitransparent and can be produced in various colours, making it possible for them to be applied in building integrated photovoltaic (BIPV) applications [3]. A typical DSSC consists of a nanocrystalline semiconductor coated photoactive electrode, an iodide based liquid electrolyte, and a counter electrode (normally platinum or

carbon-based coating on a conducting glass substrate). When the DSSC is irradiated with light, photoexcited electrons of the dye are transferred to the conduction band of TiO₂, and the oxidized dye cations are regenerated by the I[−] in the electrolyte. The I₃[−] formed in this process is reduced at the counter electrode, thus completing the cycle and generating the photocurrent [4]. I[−]/I₃[−] redox mediator shuttles between the two electrodes.

In the determination of high efficiency and long time stability of the DSSCs, electrolytes play an important role [5]. A gel polymer electrolyte has been used in this work in order to replace liquid electrolytes that may cause some practical limitations of physical and chemical stability at higher temperatures [5, 6]. The conductivity of gel type electrolytes is usually high compared to that of solid polymer electrolytes and it can be improved to be almost comparable to that of the conventional electrolyte solutions in case of high solution fraction [7]. Since the solvent is entrapped in the polymer network structure in gel electrolytes, leakage problems can

be avoided. The solvents entrapped in the polymer matrix not only improve the conductivity of electrolytes but also improve the contacts between interfaces of the electrolyte and the dye covered nanocrystalline TiO_2 surface and electrolyte-counter electrode leading to improved efficiency of DSSCs [5, 7].

Many host polymers have been used to prepare electrolytes for use in DSSCs [8–11]. In this work, chitosan has been chosen as the host polymer for the electrolyte since this polysaccharide is nontoxic and biocompatible. Chitosan is also being explored intensively for applications in pharmaceutical, cosmetics, biomedical, biotechnological, agricultural, food, and nonfood industries [12–15]. Chitosan is the deacetylated form of the chitin polysaccharide and contains the β -(1-4) linked 2-amino-2-deoxy-D-glucopyranose repeating structure [16, 17]. Chitosan is generally insoluble under normal conditions due to the presence of β -1, 4'-glycosidic linkages that gives chitosan its structural rigidity and crystalline structure besides promoting the formation of intramolecular hydrogen bonds. This limits its usage and further investigation for the biological activities and development has been restricted [18]. Since chitosan and its derivatives are favourable for many applications, chitosan should be effectively modified to fully explore its ability. The chemical modification of chitosan can provide functional groups as primary amine as well as secondary hydroxyl groups in its monomers [12].

In order to improve the solubility of chitosan in general organic solvents, *N*-phthaloylation is found to be one of the convenient methods. Kurita et al. have applied *N*-phthaloylchitosan as an organosoluble key intermediate for a series of controlled modification reactions [19–21]. Chemical introduction of some functional groups of hydrophobic nature will result in disruption of the formation of specific hydrogen bond interactions between its amino and hydroxyl groups with the solvents [22]. *N*-Phthaloylchitosan exhibits high affinity for organic solvents, namely, dimethylsulfoxide (DMSO), dimethylacetamide (DMAc), dimethylformamide (DMF), and pyridine [23]. In this work, we aim at developing a best performing DSSC using a *N*-phthaloylchitosan-based gel polymer electrolyte. Therefore, gel polymer electrolytes were prepared with various amounts of tetrapropylammonium iodide, Pr_4NI , as the salt and investigated in order to find the best composition for high conductivity. Pr_4NI has been chosen as the primary iodide salt for the electrolyte as it has been shown to produce good efficiencies in DSSCs by enhancing the iodide conductivity in the electrolyte [24, 25]. The performances of the electrolytes were tested in DSSCs based on mesoporous TiO_2 sensitized with N719 dye as the sensitizer. The performance of the best DSSC was improved further with the addition of a second iodide salt, LiI .

2. Experimental

2.1. Phthaloylation of Chitosan. The synthesis procedure used in this work is similar to that reported by Nishimura et al. [22]. Chitosan (Aldrich) and phthalic anhydride (Aldrich) were refluxed between 100°C and 120°C under nitrogen atmosphere for 6 h in dimethylformamide (DMF) purchased

TABLE 1: Pr_4NI content of different electrolyte samples.

Samples	PhCh/g	$\text{Pr}_4\text{NI/g}$
1	0.1	0.02
2	0.1	0.04
3	0.1	0.06
4	0.1	0.08
5	0.1	0.10
6	0.1	0.12
7	0.1	0.14
8	0.1	0.16

TABLE 2: Composition of the salts in binary salt electrolytes.

Samples	$\text{Pr}_4\text{NI/g}$	LiI/g
A	0.12	0.00
B	0.10	0.02
C	0.08	0.04
D	0.06	0.06
E	0.04	0.08

from R & M Chemicals. The temperature was then reduced to 60°C , and the mixture was left overnight. The product of reaction between chitosan and phthalic anhydride dissolved in DMF is a yellowish solution. This solution was poured into ice water to precipitate the product, *N*-phthaloylchitosan. The precipitate was collected and washed with distilled ethanol (from J. T. Baker) in a soxhlet extractor for 8 h. The final product was dried in vacuum at 60°C for about 6 h.

2.2. Preparation of Gel Polymer Electrolyte (GPE). Fixed amounts of ethylene carbonate (0.2 g) and propylene carbonate (0.2 g) from Aldrich were stirred well in a closed glass container with the relevant weights of Pr_4NI (see Table 1). 0.1 g of phthaloylchitosan was then added to each salt solution. The mixture was heated to 150°C and stirred until the mixture becomes a homogeneous gel. Then heater was stopped and the solution was allowed to cool down to room temperature. Iodine (10 wt.% of salt) was then added to the gel polymer electrolyte and stirred until the solution becomes homogeneous. The impedance of the resulting gel polymer electrolyte was then measured.

To the most conducting gel polymer electrolyte (Sample 6), lithium iodide, LiI , was added in such a way that the total weight of the iodide salts remains the same (0.12 g) in all the electrolytes. The salt compositions used in the electrolytes are shown in Table 2.

2.3. Device Assembly. Fluorine tin oxide (FTO) glasses (from Solaronix SA), which were used as the substrates, were rinsed with distilled water and ethanol before use. For preparing TiO_2 layer on the substrate, TiO_2 colloidal suspension was prepared by grinding 0.5 g powder of TiO_2 with 2 mL of HNO_3 , 0.1 g of carbowax, and few drops of surfactant octylphenol ethylene oxide condensate (Triton X-100) in an agate mortar. The TiO_2 colloidal suspension was spread on

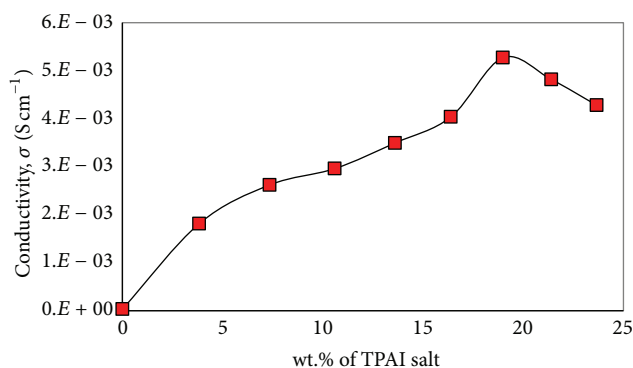


FIGURE 1: Effect of Pr_4NI concentration on the conductivity at 25°C.

the clean (FTO) glass by applying the doctor blade technique. The TiO_2 electrode was sintered in a furnace at 450°C for 45 minutes. The TiO_2 electrode was cooled down to about 60°C and then dipped in a warm ethanol solution of Ruthenium dye (N719) for 24 hours for dye adsorption.

The photovoltaic performance of DSSCs was investigated using a LOT-Oriel solar simulator (1.5 AM, 1000 W m $^{-2}$) and a computer controlled eDAQ Potentiostat. From the J - V (current density-cell potential) characteristic curves, the short-circuit current (J_{SC}) and open circuit voltage (V_{OC}) were obtained and the fill factor (FF) and energy conversion efficiency (η) were calculated from the following equations:

$$\text{FF} = \frac{J_{\text{max}} \times V_{\text{max}}}{J_{\text{SC}} \times V_{\text{OC}}}, \quad (1)$$

$$\eta = \frac{P_{\text{out}}}{P_{\text{in}}} \times 100 = \frac{J_{\text{SC}} \times V_{\text{OC}} \times \text{FF}}{P_{\text{in}}} \times 100,$$

where J_{max} is the current density at maximum power output, V_{max} is the voltage at maximum power output, and P_{in} is the power of the incident light.

3. Results and Discussion

Figure 1 shows the variation of conductivity at room temperature for the phthaloylchitosan-based gel polymer electrolytes with various Pr_4NI salt compositions. The conductivity of the electrolyte with the lowest Pr_4NI concentration, 3.8 wt.%, is $1.81 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C. With increasing amount of Pr_4NI salt up to 19.0 wt.% in gel polymer host, the ionic conductivity increases until a maximum conductivity of $5.27 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C. On increasing the Pr_4NI concentration further, the conductivity is observed to decrease.

This behavior of the conductivity can be attributed to the change in the amount of mobile ions in the gel electrolytes [26]. The increase in number of mobile ions due to the increased salt dissociation with the increasing amount of salt in the electrolyte can result in the conductivity increase. The Pr_4NI salt molecules are expected to dissociate into Pr_4N^+ cations and I^- anions in the GPE. As the Pr_4N^+ cations are bulky they are expected to have sluggish movement or get trapped in the polymer matrix and therefore ionic

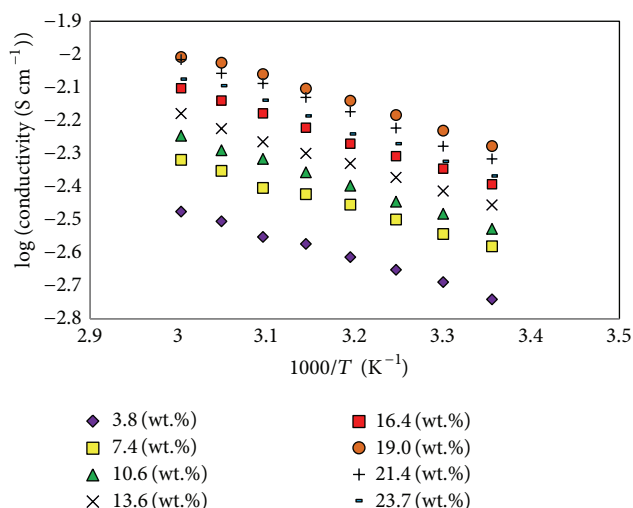


FIGURE 2: Temperature dependence of conductivity for phthaloylchitosan doped with different wt.% of Pr_4NI salt.

conductivity mainly comes from the I^- ions. Initially as the salt concentration increases, since dissociated ions are less, both I^- ions and Pr_4N^+ ions can be expected to be mobile and contribute to ionic conduction and the conductivity rises sharply. On further increase of salt content, the number of both Pr_4N^+ ions and I^- ions increases but the mobility of Pr_4N^+ ions is hindered due to entanglement in the polymer matrix and I^- ions may be main contributor to the conductivity. Therefore, the conductivity increases only slightly with further increase in salt content up to about 16.4 wt.% of salt. Beyond this concentration of the salt the conductivity again rises sharply due to the increase in iodide ions coming from increased salt dissociation and increased added iodine amount, which is 10 wt.% of iodide salt, giving the maximum conductivity at 19 wt.% of salt content. At 21.4 wt.% and 23.7 wt.% of Pr_4NI , ion association may have taken place in the system as the conductivity begins to decrease. In addition, conductivity can drop due to blocking effects imposed by the undissociated salt or due to higher ion aggregates present in the electrolyte at high salt concentrations.

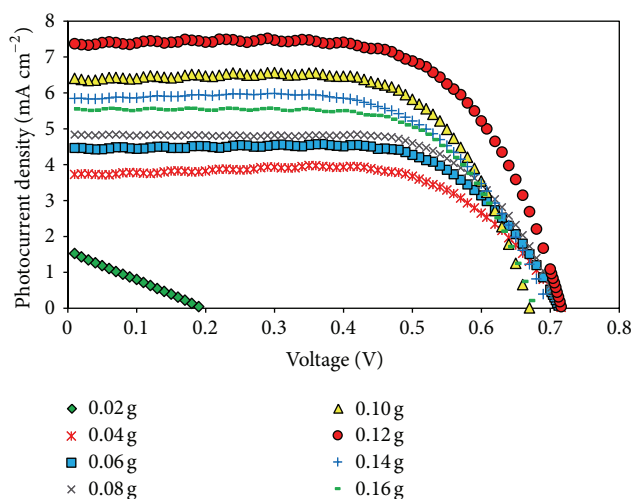
The conductivity-temperature relationship of phthaloylchitosan-EC-PC electrolytes with different amounts of Pr_4NI is exhibited in a plot of $\log \sigma$ versus $1000/T$ shown in Figure 2. It is observed that the conductivity of each electrolyte increases as the temperature is increased from 25°C to 60°C. The variations of ionic conductivity with temperature for the polymer electrolytes obey Arrhenius law, suggesting that the conductivity is thermally activated. The Arrhenius model employed in describing the temperature dependence of conductivity is as follows:

$$\log \sigma = \log \sigma_0 - \frac{0.4342E_a}{kT}, \quad (2)$$

where σ_0 is the preexponential factor, E_a is the activation energy of ionic conduction, k is the Boltzmann constant, and T is temperature in Kelvin.

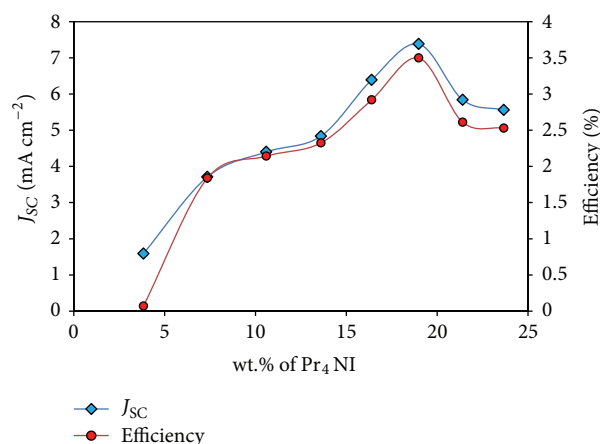
TABLE 3: Performance parameters of DSSCs with phthaloylchitosan-based electrolytes containing various salt contents.

wt.% of Pr ₄ NI	V _{max} /V	J _{max} /mA cm ⁻²	V _{oc} /V	J _{sc} /mA cm ⁻²	FF	η/%
3.8	0.10	0.78	0.19	1.59	0.26	0.07
7.4	0.51	3.54	0.68	3.24	0.69	1.79
10.6	0.53	4.04	0.71	4.40	0.69	2.14
13.6	0.52	4.44	0.71	4.84	0.67	2.32
16.4	0.48	6.08	0.67	6.39	0.68	2.92
19.0	0.52	6.70	0.72	7.38	0.66	3.50
21.4	0.50	5.20	0.70	5.84	0.64	2.61
23.7	0.51	4.94	0.67	5.56	0.68	2.53

FIGURE 3: Photocurrent density variation with cell potential for dye-sensitized solar cells having phthaloylchitosan-based electrolyte with various Pr₄NI/I₂ contents.

The electrolytes with various amounts of Pr₄NI were employed in DSSCs sensitized with N719 dye and the photocurrent density versus cell potential (*J*-*V*) characteristics were obtained under light irradiation of 100 mW cm⁻² at room temperature. The *J*-*V* curves for the DSSCs are shown in Figure 3. Very poor solar cell performance is shown by the DSSC with the electrolyte containing 3.8 wt.% of Pr₄NI. This can be due to the poor conductivity and the low density of redox mediators in the electrolyte. However with increasing amount of iodide salt together with increasing iodine content in the electrolyte, better solar cell performance is observed as can be seen from the *J*-*V* characteristic curves. The performance parameters for the DSSCs obtained from the *J*-*V* curves shown in Figure 3 are given in Table 3. The cell with electrolyte having 19.0 wt.% of Pr₄NI shows both the highest values of V_{OC} = 0.72 V and J_{SC} = 7.38 mA cm⁻². Electrolyte with the lowest salt content of 3.8 wt.% shows the lowest values of V_{OC} and J_{SC} of about 0.19 V and 1.59 mA cm⁻², respectively.

In addition to V_{OC} and J_{SC}, the performance of the DSSCs is reflected by the parameters of fill factor (FF) and energy conversion efficiency (η). The calculated values of FF and η are summarized in Table 3. The DSSC fabricated using

FIGURE 4: Effects of weight percentage of Pr₄NI salt in the electrolyte on efficiency and short-circuit photocurrent density of DSSCs.

the electrolyte containing 19.0 wt.% of Pr₄NI with η of 3.50 exhibits fill factor of 0.66. The highest fill factor was obtained for the DSSC that had the electrolyte containing 19.0 wt.% of Pr₄NI. This can be attributed to the combined effect of series resistance and shunt resistances as reported in [26]. In a DSSC, low shunt resistance provides a substitute path for light generated current and hence lowers the power output which in turn decreases the fill factor. As series resistance in the DSSC is usually lower when compared to conventional solar cells, improved fill factor is expected.

The relationships between Pr₄NI content in the electrolyte with efficiency and short-circuit current density are shown in Figure 4. Efficiency of the cells is observed to increase with the Pr₄NI content until 19.0 wt.% of Pr₄NI and further increase of salt decreases the efficiency. Thus the cell with 19.0 wt.% of Pr₄NI shows the highest efficiency value of 3.5%, the highest value obtained with the single iodide salt polymer electrolyte system used in this work. The efficiency variation shown in Figure 4 correlates with the conductivity variation shown in Figure 1. Figure 4 also shows that the short-circuit current density of DSSCs increases with increasing concentration of the salt up to 19.0 wt.% of Pr₄NI. It can be seen that the variation of efficiency of the cells is parallel with variation of short-circuit current density as well as the conductivity of the electrolyte with the salt content. The short-circuit current of the cell is governed by the ionic

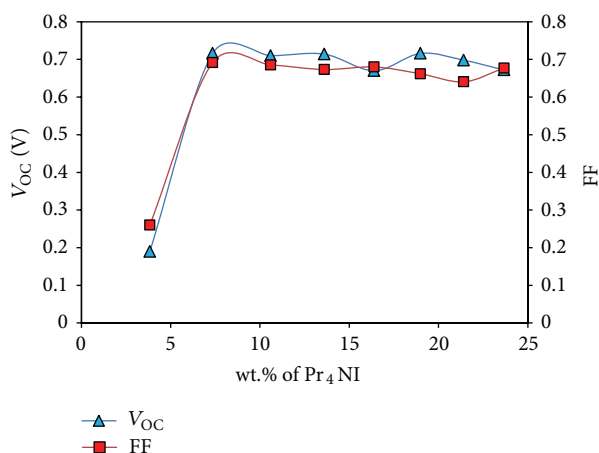


FIGURE 5: Effects of weight percentage of Pr₄NI salt in the electrolyte on open circuit voltage and fill factor of DSSCs.

conductivity dominated by the transport of I^-/I_3^- redox couple as exhibited by a comparable PAN based electrolyte system using the same salt and plasticizers [27]. As explained earlier, the iodide ions are the main contributors to the ionic conductivity in the GPE used. Since iodides (I^-/I_3^-) play a major role in determining the current in DSSCs, the J_{SC} should follow the variation of free iodide ions content in the electrolyte and therefore must increase sharply as the salt content increases as more and more iodide ions are expected to be produced due to salt dissociation. According to the results in Figure 1, the number of iodide ions increases up to 19 wt.% of salt and the number decreases beyond this salt content due to possible ion association taking place. Hence the J_{SC} is expected to follow this trend. But in Figure 4, as the salt content increases, J_{SC} increases sharply at the beginning up to 7.4 wt.% of salt and beyond 13.6 wt.% up to 19 wt.% of salt content. The increase becomes less steep for the salt contents between 7.4 and 13.6 wt.%. It should be noted that the current in the DSSC is not only controlled by the iodide conduction in the electrolyte but also controlled by the electron injection rate from the dye molecules to TiO₂ and the recombination rate of injected electrons with the iodide ions in the electrolyte. The injection rate is also affected by the cations as they can stick to the TiO₂ surface and shift the Fermi level. The combined effect of all these processes results in the observed variation of J_{SC} with salt content. Further experiments and analysis are needed to explain the exact correlation between ionic conductivity and the J_{SC} .

To our best knowledge, the J_{SC} and efficiency values obtained in this study for DSSC containing 19.0 wt.% of Pr₄NI are the highest values reported so far for a quasisolid state DSSC having chitosan host polymer based electrolyte system with a single iodide salt.

The dependence of V_{OC} and FF on the weight percentage of Pr₄NI salt in the electrolyte is shown in Figure 5. The V_{OC} and FF show similar variations but different to that shown by J_{SC} in Figure 4. These results show that the efficiency variation of the DSSCs is determined mainly by the changes in J_{SC} .

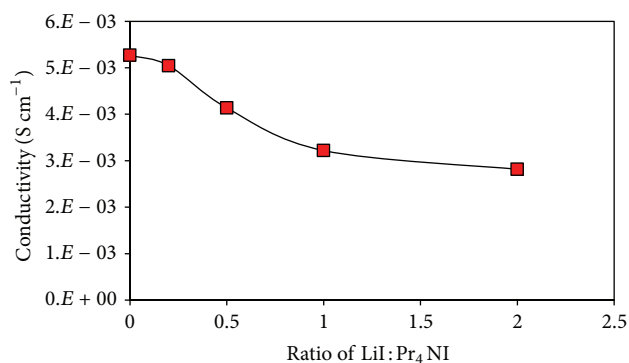


FIGURE 6: Effect of various LiI : Pr₄NI compositions on the conductivity.

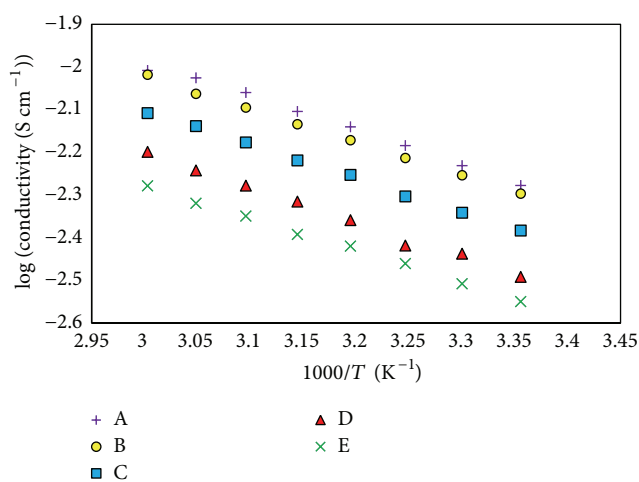
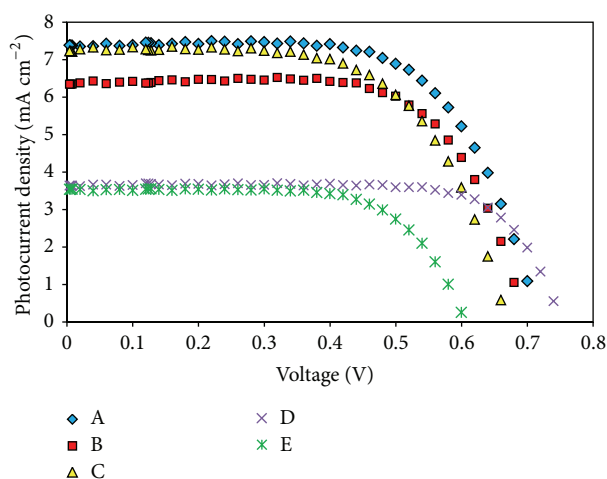


FIGURE 7: Temperature dependence of conductivity for phthaloylchitosan-based electrolyte containing different ratio of LiI : Pr₄NI binary salt.

It has been reported that the addition of small cations such as Li⁺, K⁺, and Mg²⁺ to the gel polymer electrolytes so as to have two mixed cations in the electrolyte improves the solar cell performance [28–30]. In particular these small cations adsorbed onto the TiO₂ surface alter the flat band potentials so as to improve the charge injection rates from excited dye molecules to the TiO₂ enhancing the photocurrent [31]. Hence in order to improve the photocurrent density of the DSSC various amounts of lithium iodide (LiI) have been added to the most conducting polymer electrolyte, that is, phthaloylchitosan with 19.0 wt.% of Pr₄NI. Figure 6 shows the room temperature ionic conductivity variation of the gel polymer electrolyte for different mass fractions of the LiI and Pr₄NI. The conductivities of gel polymer electrolytes with various compositions of LiI : Pr₄NI at different temperatures are shown in Figure 7. With the addition of LiI conductivity drops are observed at all temperatures in the measured temperature range. This conductivity drop can be attributed to the reduction of polymer flexibility due to inter- and intramolecular cross links by Li⁺ due to its high charge density. The reduction of polymer flexibility can

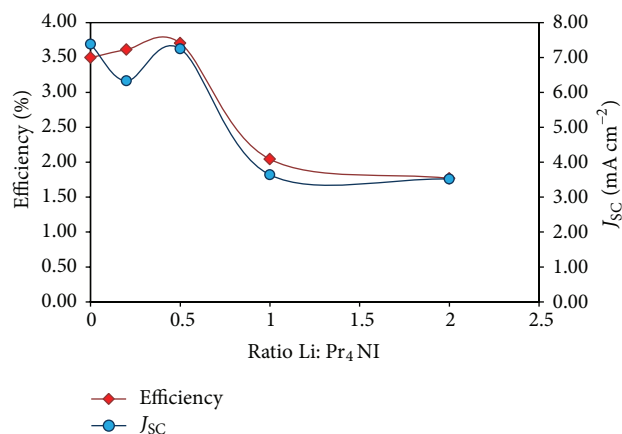
TABLE 4: The performance parameters of DSSCs with different gel polymer electrolytes.

Electrolyte samples	V_{\max}/V	$J_{\max}/\text{mA cm}^{-2}$	V_{oc}/V	$J_{\text{sc}}/\text{mA cm}^{-2}$	FF	$\eta/\%$
A	0.52	6.70	0.72	7.38	0.66	3.50
B	0.60	6.02	0.80	6.33	0.72	3.61
C	0.57	6.50	0.77	7.25	0.67	3.71
D	0.61	3.35	0.75	3.64	0.75	2.04
E	0.53	3.35	0.70	3.52	0.71	1.77

FIGURE 8: Photocurrent-voltage curves of DSSCs with phthaloylchitosan based electrolyte different ratio of LiI : Pr₄NI binary salt.

increase the local viscosity of electrolyte medium hindering mobility of charge carriers. As can be seen from Figure 7, the temperature dependence of conductivity for all electrolytes approximately obeys the Arrhenius relationship as observed in other polymer systems [32].

As expected the incorporation of small amount (less than 0.04 g) of LiI into the electrolyte has improved the solar cell performance (see Figure 8) even though these electrolytes have shown a slight decrease in conductivity as shown in Figure 6. The DSSC parameters for the devices having the binary salt system are tabulated in Table 4. The efficiency reaches a maximum value of 3.71% for a combination of 0.08 g Pr₄NI and 0.04 g LiI in the electrolyte. This increase in efficiency can be attributed to the mixed cation effect as observed with many binary salt electrolytes [29, 30]. Mixed cation effect is observed when binary iodide salts having smaller and larger cations are present in the gel electrolyte. The smaller cations get adsorbed to the TiO₂ and reduce the Fermi level in such a way to improve the electron injection and, at the same time, the number of iodide ions in the electrolyte increases due to the addition of LiI salt and both these effects increase the current in the DSSC. However, higher amounts of added LiI (more than 0.04 g) have reduced the solar cell efficiency due to the ionic conductivity drop as explained above. Variations of efficiency and photocurrent density with different ratio of Pr₄NI : LiI are shown in Figure 9. The efficiency variation closely follows that of the current density variation.

FIGURE 9: Dependence of J_{sc} and η of DSSCs with different gel polymer electrolytes.

4. Conclusions

In this work, a gel polymer electrolyte has been successfully prepared using phthaloylchitosan as the polymer host and it has been used to produce high performance in a dye-sensitized nanocrystalline solar cell. The most conducting polymer electrolyte containing 19.0 wt.% of Pr₄NI exhibited the highest efficiency of 3.5% with J_{sc} of 7.38 mA cm⁻², V_{oc} of 0.72 V, and FF of 0.66. The efficiency of the DSSC was further improved to 3.7% when part of the Pr₄NI salt in the electrolyte is replaced with LiI salt (Pr₄NI : LiI = 2 : 1) with the value of J_{sc} , V_{oc} and fill factor of 7.25 mA cm⁻², 0.77 V and 0.67, respectively. The presence of the LiI in addition to the Pr₄NI improves the charge injection rates and increases the iodide contribution to the total conductivity and both factors contribute to the increase in efficiency of the DSSC.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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