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Influence of Solvents of Redox Electrolyte on DSSC Performance

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ABSTRACT

Attempts to improve the light-to-electrical power conversion efficiency of Dye sensitized solar cells (DSSC) has come out with variety of liquid electrolytes. DSSC comprise of a dye-adsorbed TiO_2 layer fabricated on transparent conducting oxide (FTO) acting as photo anode, platinum coated on FTO as the counter electrode along with an iodide/triiodide redox electrolyte. Iodide/ triiodide redox electrolyte is found to be unique as far as the DSSC is concerned. Present work reports on comparative study on different solvents for the iodide/ triiodide redox electrolyte with natural dye from pomegranate as photosensitizer. An attempt is made to evaluate the effect of mixing of natural additives with the standard electrolyte and the results are found to be encouraging. Characterization of fabricated cell is done using keithley source measuring unit and solar cell software, and parameters such as open circuit voltage, short circuit current, fill factor, and efficiency were evaluated under natural sun. It is observed that natural electrolyte tends to facilitate the mobility of carriers, leading to increase in the efficiency of the cell. Variation of cell performance with intensity of light is also studied with the best solvent identified.

KEY WORDS

DSSC, Natural electrolyte, Redox electrolyte

INTRODUCTION

Dye-sensitized solar cells (DSSC) are a relatively new class of photovoltaic device with a lot of remarkable properties. DSSC is pervasive for its ease of fabrication, low cost and dynamic optical properties. Dye sensitized solar cells is based on the photosensitization of wide band gap metal oxide semiconductors. DSSC consist of a dye-adsorbed TiO_2 layer fabricated on transparent conducting oxide (FTO), acting as photo anode and platinum coated on FTO as the counter electrode. Iodide/triiodide redox electrolyte is loaded between these two electrodes. The dye adhered on nano crystalline oxide film helps in harvesting sunlight [1]. The most efficient groups of dye are Ruthenium complexes and porphyrin derivatives [2]. Recently many new dyes have been synthesized to get record efficiency [3]. Even though dye plays the major role in the process of absorbing photons to create free carriers, the redox electrolyte also has also a significant role in increasing the overall photo conversion efficiency of solar cell. They act as a mediator in dye regeneration and charge transport between the photo anode and cathode. The liquid redox electrolyte consists of a redox mediator, additives and a solvent. It is with the help of redox electrolyte that the dye regains its original electronic structure and thereby makes it available for further photo cycles. Thus electrolyte acts as a mediator that electrically connects photo anode to counter electrode.

It is observed that nature of solvent in the electrolyte can influence the efficiency of DSSC. Organic solvents and ionic liquids are the two major liquid electrolyte solvents. Various types of nitriles have also been reported. Based on the overall conversion efficiency, acetonitrile (AN) have shown to be the most successful and efficient organic solvent. The main reason for this performance shown by acetonitrile may be due to its low viscosity and good ability to dissolve organic components, salts as well as additives in electrolytes. Maximum reported conversion efficiencies of 12% have been achieved using AN-based electrolytes[4,5]. Redox electrolyte used in DSSC must satisfy certain electrochemical conditions. It must have poor visible light absorption, fast electron transfer kinetics at counter electrode and good photo electrochemical stability. Leakages of electrolyte, volatilization of solvent and thermal instability are some of the other factors that diminish the long term performance of DSSC [6, 7, 8].

Principle behind DSSC is that when a photon strikes on to the dye molecules, the dye gets excited. From the excited state, the dye loses an electron to the conduction band of titanium dioxide and it gets oxidized. From the TiO_2 semiconductor the electrons are transported over the conductive surfaces of the FTO/glass electrode and over to the load and back to the counter electrode. The platinum counter electrode now transfers the electron to the redox couple which finally regenerates the dye again for the next photo cycle.

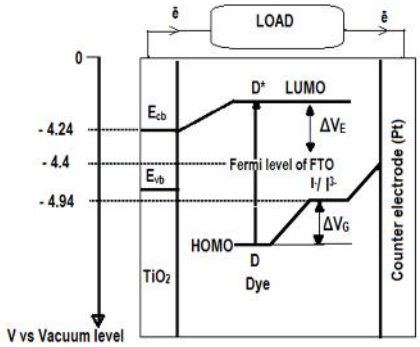

Fig 1: Energy level diagram of DSSC

Figure 1 shows energy levels suitable for the working of DSSC [9]. For efficient electron injection the electrochemical potential of the LUMO state of the dye should be more positive than the conduction band of TiO_2 which is at - 4.24 V with respect to vacuum level and a potential difference of 0.2 V is desirable [10]. Similarly the electro chemical potential of HOMO level of dye should be at a more negative potential than the I^-/I_3^{3-} redox system for efficient regeneration of the dye [11]. Potential of I^-/I_3^{3-} redox system is - 4.94 V with respect to vacuum level as shown in Fig 1. The first oxidation potential obtained from cyclic voltammetry can be co-related to HOMO energy level of the dye [12]. It is also an accepted fact that optical absorption energy when added to HOMO energy level will result in LUMO energy level of the dye [13]. In one of our earlier reports a similar study was carried out with natural dyes [14]. Based on the results we have chosen natural dye from pomegranate as photosensitizer. In this work, we have tried to evaluate the performance of this dye with various solvents and various natural additives. Thus novel attempt has been made to optimize the redox electrolyte with a natural dye.

EXPERIMENTAL

1gm of TiO_2 nano powder (particle size < 25 nm) is dispersed in 2ml of acetic acid by grinding in a mortar. Three drops of Triton X-100 (surfactant) are added to lower the surface tension of the colloid in order to facilitate easier spreading onto the conducting glass plate[15]. Composition of the paste was found to be an important factor for uniformity of the layer. We adopted doctor blade technique and used a glass rod to spread titania paste onto the glass. The paste is smeared on a glass substrate immobilized by an adhesive tape strip, which determines the film thickness. In the present case, film thickness is around 6µm. After drying, it was annealed at 450 ^{0}C for one hour in muffle furnace[16]. Natural dye is adsorbed onto this TiO_2 surface by immersing it in dye solution for 12 to 18 hour at room temperature. Excess dye was washed off by dipping it in ethanol. This dye/ TiO_2/FTO/ glass structure forms the photo anode for DSSC. Platinum coated glass with resistance in the order of few ohms was used as the counter electrode for DSSC.

Selected solvents for iodide/ triiodide redox electrolyte are acetonitrile, ethylene glycol and water. 0.5 M potassium iodide (KI) and 0.05 M iodine is added to the selected solvent (25 ml of acetonitrile or 10 ml of ethylene glycol). It is stirred well and stored in a dark container. In the case of water based electrolyte 0.01 N iodine solutions was added to 0.1 M potassium iodide in equal proportions. Natural extracts from turmeric, tamarind, ginger, lemon and coconut water were filtered / centrifuged and used as additives in the redox electrolyte.

Instrumentation and software:-Kethiley Source Measuring Unit (model 2401) and solar cell characterization software were used for characterization of the cell. Solar cell parameters such as open circuit voltage (Voc), short circuit current (Isc), fill factor (FF) and efficiency of the cell were analyzed. All the photo response studies were carried out under diffused natural sunlight. The intensity of diffused sunlight was measured using watt meter and the intensity was maintained at $100W/m^2$ by varying the position of the experimental setup with respect to direct sunlight. The active area of all the cells was restricted to $0.25\ cm^2$ by proper masking.

RESULTS AND DISCUSSION

Effect of different solvents for iodine redox electrolyte

Cell with structure glass/FTO/TiO_2/natural dye/ (I^-/I^3) electrolyte/Pt/glass was studied under diffused natural sunlight. A medium low intensity of 100 W/m^2 was chosen as the fixed illumination level. V-I characterization was carried out to understand the performance of the cell with iodine redox electrolyte in two different organic solvents (viz. acetonitrile and ethylene glycol) and in aqueous medium. The characteristic curve of the cells is shown in Fig.2. Table 1 shows the numerical value of important cell parameters.

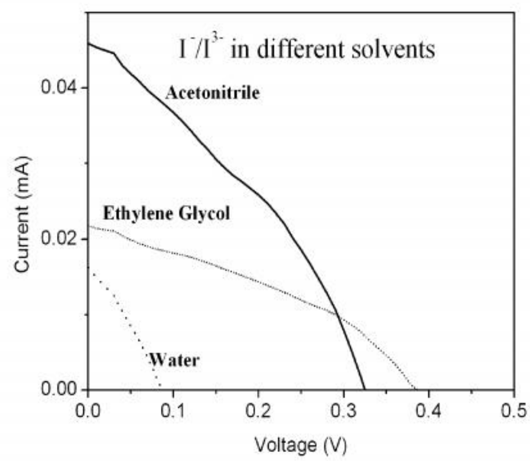

Fig 2: V-I graph of different solvents for I^-/I^{3-}electrolyte based DSSC

Table 1. Cell parameters with different solvents

Solvent	V_{oc} (V)	I_{sc}(A)	Fill factor	Efficiency
Acetonitrile	3.24E-01	4.86E-05	3.36E-01	2.12E-01
Ethylene Glycol	3.85E-01	2.26E-05	3.47E-01	1.21E-01
Water	8.54E-02	1.75E-05	2.91E-01	1.74E-02

Results show that I^-/I^{3-}electrolyte in acetonitrile solvent is showing the best performance of maximum closed circuit current (around 0.05 mA for a cell area of 0.25 cm^2). Even though the open circuit voltage (Voc) with this solvent is slightly less than that with ethylene glycol it is seen that efficiency is maximum for acetonitrile. The performance of aqueous solvent is found to be poor in all respects like Isc, Voc, FF and efficiency. Hence for further studies the combination of electrolyte with acetonitrile was given more importance.

As far as any solar cell is concerned the performance of the cell with respect to incident light intensity is an important factor. Fig 3 shows the V-I performance of the acetonitrile

based cell under various light intensities. It is interesting to note that the decrease in Isc and Voc is very less when the intensity is reduced from 200 W/m^2 to 50 W/m^2 (i.e. when intensity is reduced by 75%).

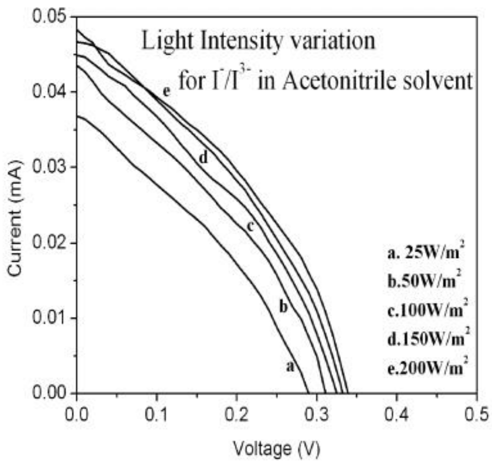

Fig 3: V-I graph of DSSC showing the effect of intensity variation on I^-/I^{3-}electrolyte in acetonitrile solvent

Effect of additives to iodine redox electrolyte

The effect of adding various natural extracts as additives to the electrolyte was studied in detail. The additives included extracts from natural sources like turmeric, tamarind, ginger, lemon, and coconut water. In this study acetonitrile was chosen as the solvent for I^-/I^{3-}redox electrolyte. This study was conducted at a low intensity of 50W/m^2, Fig.4.

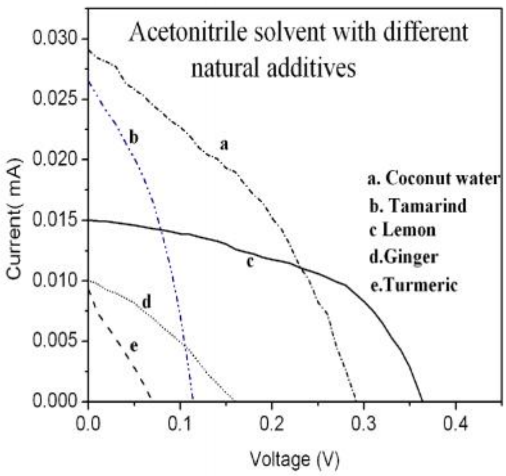

Fig 4: V-I graph of DSSC in acetonitrile solvent with different natural additives

The results are consolidated in Table 2. The performance of turmeric and ginger was very poor. Though tamarind gave a high Isc the Voc recorded was not appreciable and hence the efficiency was poor. Coconut water also showed appreciable performance. It was the extract from lemon that gave the best FF and V_{oc} of above 0.35 V for the small area of 0.25cm^2. Hence it can be concluded that the addition of lemon extract to electrolyte is enhancing the performance of the cell considerably. The fill factor has shown a significant improvement along with slight increase in efficiency. This effect might be due to enhanced mobility of charge carriers leading to fast regeneration of the oxidized dye in the presence of citric acid contained in the lemon extract.

Table 2. V-I parameters of various acetonitrile based cells with different additives and no additive

Solvent	Additive	V_{oc}(V)	I_{sc}(A)	Fill factor	Efficiency
Acetonitrile	Coconut Water	2.92E-01	2.91E-05	3.68E-01	2.49E-01
Acetonitrile	Tamarind extract	1.14E-01	2.65E-05	3.81E-01	9.22E-02
Acetonitrile	Lemon extract	3.67E-01	1.50E-05	4.94E-01	2.6 1E-01
Acetonitrile	Ginger extract	1.59E-01	1.04E-05	3.06E-01	4.85E-02
Acetonitrile	Turmeric extract	6.95E-02	9.34E-06	2.49E-01	1.29E-02
Acetonitrile	No additive	3.10E-01	4.36E-05	3.41E-01	2.48E-01

In order to find out the best volume ratio of acetonitrile and lemon extract, a V-I series was carried for various concentrations. It was observed that the best fill factor along with efficiency was obtained for equal volume ratio of acetonitrile and lemon extract, as shown in Fig.5.

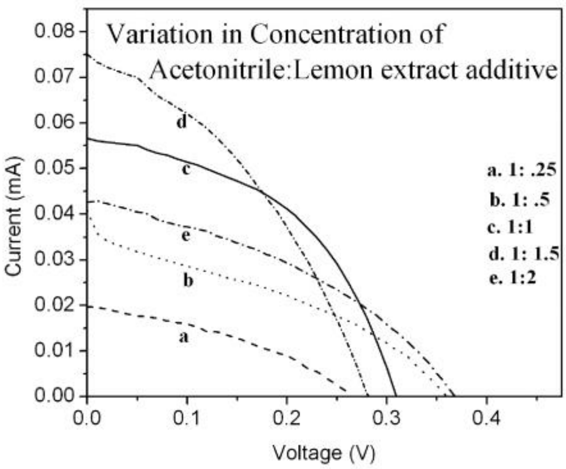

Fig 5: V-I graph of cells with various volume ratio of acetonitrile and lemon extract

SUMMARY

Dye sensitised solar cell with a fixed area of 0.25cm^2 having structure electrode/TiO_2/natural dye/ (I^-/I^3) electrolyte/counter electrode was studied under diffused natural sunlight. The sensitiser dye used for this study was the natural extract from pomegranate fruit. The best solvent for this natural dye was found to be acetonitrile and the efficiency of the cell was around 0.2%. Natural extracts from turmeric, tamarind, ginger, lemon and coconut water was tried as additive to I^-/I^3 electrolyte. Addition of lemon extract was found to slightly enhance the efficiency of the cell and the fill factor reached up to nearly 0.5. This result might be due to enhancement of mobility of carriers in the presence of citric acid contained in lemon extract. The intensity study reveals that, DSSC works well in diffused sun light. Thus adding solvents with proper additives in redox electrolyte will improve the performance of solar cell.

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