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Research Article

Performance of Dye-Sensitized Solar Cells with (PVDF-HFP)-KI-EC-PC Electrolyte and Different Dye Materials

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A plasticized polymer electrolyte system composed of PVDF-HFP, potassium iodide (KI), and equal weight of ethylene carbonate (EC) and propylene carbonate (PC) has been used in a dye-sensitized solar cell (DSSC). The electrolyte with the composition 40 wt. % PVDF-HFP-10 wt. % KI-50 wt. % (EC + PC) exhibits the highest room temperature ionic conductivity of $1.10 \times 10^{-3} \text{ S cm}^{-1}$. A small amount of iodine crystal of about 10 wt. % of KI was added to the electrolyte in the liquid state to provide the redox couple for DSSC operation. The polymer electrolyte films were prepared by the solvent casting method. The DSSCs were fabricated with the electrolyte film sandwiched between a TiO_2 /dye photoelectrode and a Pt-counter electrode and characterized under 100 mW cm^{-2} white light. The DSSC performance with different dyes such as Ruthenizer 535 (N3), anthocyanin, chlorophyll, and a mixture of anthocyanin and chlorophyll ($v/v = 1$) has been compared. The DSSC with Ruthenizer 535 (N3) dye exhibits the best performance with a short-circuit current density of 8.16 mA cm^{-2} , open-circuit voltage of 0.76 V, fill factor of 0.35, and photoconversion efficiency of 2.2%.

1. Introduction

Solar cells are devices that utilize energy from the sun by converting solar radiation directly into electricity. The conventional solar cell device is silicon-based solar cells with efficiency as high as 30% under concentrated light. However, high manufacturing cost prevents the widespread use of silicon cells [1, 2]. Dye-sensitized solar cells (DSSCs) have attracted much attention as they can also offer high-energy conversion efficiencies. DSSCs are easy to fabricate, and manufacturing cost is lower compared to silicon solar cells [3–5]. The structure of the DSSC consists of a TiO_2 photoelectrode coated on conducting glass, dye sensitizer, an electrolyte containing redox couple, and a counter electrode [6]. Energy conversion in a DSSC is based on the injection of an electron from a photoexcited state of the dye into the conduction band of the TiO_2 photoelectrode [7]. Since the dye plays an important role in harvesting light and solar energy conversion to electricity, efforts have been focused on dye materials. The commercial synthetic ruthenium (II) polypyridyl complexes such as N719 and N3 are widely used in DSSCs

due to the satisfactory photoelectric conversion efficiency up to 10% [8, 9]. However, these dyes use metal compound complexes, which are expensive and produce environmental pollution [10]. Another approach is to use natural dyes, which is environmentally friendly, nontoxic, biodegradable, and cheaper compared to the synthetic dyes, but has yet to show good performance in terms of efficiency [11]. Natural sensitizing dyes include anthocyanins [12, 13]. In this study, the DSSCs were prepared with N3 dye or natural dyes. Anthocyanin from black rice extraction was used as the dye since anthocyanin has good chemical bonding with titanium dioxide [14]. Chlorophyll, a natural photosensitizer for photosynthesis in green plants, is another attractive potential compound as photosensitizer in the visible region for DSSC [15, 16].

2. Experimental

2.1. Materials. Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) of MW 400,000 and potassium iodide (KI) salt were procured from Aldrich. High-purity (99%)

TABLE 1: Different compositions of PVDF-HFP polymer electrolyte.

Sample	Electrolyte composition in wt.% ratio		Weight (g)			Iodine (g) (10% of KI)
	(PVDF-HFP:KI):(EC/PC)	PVDF-HFP	KI	EC/PC		
S0	(50:0):50	1.00	0.00	1.00	0.00	
S1	(45:5):50	0.90	0.10	1.00	0.01	
S2	(40:10):50	0.80	0.20	1.00	0.02	
S3	(35:15):50	0.70	0.30	1.00	0.03	
S4	(30:20):50	0.60	0.40	1.00	0.04	

acetone, ethylene carbonate (EC), and propylene carbonate (PC) were purchased from Fluka and TiO₂ paste PST-18NR from JGC Catalyst and Chemicals Ltd., Japan. Compact layer solution, *di-isopropoxytitanbis(acetylacetonate)* was purchased from Aldrich and was diluted with ethanol to obtain 0.38 M. Ruthenizer 535 (N3) dye, purchased from Solaronix, Switzerland was diluted to 0.003 M with ethanol and *chloroplatinic acid* was diluted to 0.005 M in 2-propanol prior to use. The *chloroplatinic acid* was purchased from Aldrich.

2.2. Preparation of Polymer Electrolytes. The electrolyte system using PVDF-HFP as polymer host, potassium iodide (KI) salt, and a mixture of ethylene carbonate (EC) and propylene carbonate (PC) at 1:1 weight ratio as plasticizers has been prepared for application in DSSC. Several compositions by weight % ratio of (polymer:salt):(plasticizer) were prepared as listed in Table 1. Acetone was used to dissolve the polymer, salt, and the plasticizer at 40°C, and the liquid solutions were cast to form electrolyte films. Electrochemical impedance spectroscopy (EIS) technique was used to determine the conductivity of each composition. The highest conducting electrolyte was used to fabricate the DSSC.

2.3. Preparation of Dye Materials. Three types of dyes were prepared for this study. First, chlorophyll dye was prepared from 20 g fresh leaves of fragrant screwpine (*Pandanus amaryllifolius*) or locally known as *pandan leaves*. The leaves were cleaned with distilled water, rinsed with ethanol, and were cut into small pieces and immersed in 200 mL ethanol. Second, anthocyanin dye solution was prepared from 100 g black rice immersed in 100 mL ethanol. Both solutions were kept for 24 hours in the dark before filtration to remove residues. Third, to obtain 0.003 M N3 dye, 10 mg Ruthenizer 535 (N3) dye powder was diluted in 5 mL ethanol and kept for 24 hours in the dark before use.

2.4. Preparation of Electrodes. The working electrode is a TiO₂ layer, and the counter electrode is a platinum layer. Indium tin oxide (ITO) glass was used as a substrate for both electrodes. To prepare the working electrode or photoanode, TiO₂ paste was doctor bladed on the ITO surface [17–19]. Prior to this, the ITO glass has been spin-coated with *diisopropoxytitanium bis(acetylacetonate)* at 3000 rpm for 10 seconds to improve adhesion of TiO₂ on the ITO glass and provide a larger TiO₂/ITO contact area. This compact layer also minimizes contact between the redox electrolyte and the conductive ITO surface. This is necessary to prevent electron

recombination in the DSSC and hence improve efficiency [20]. The layers were sintered at 450°C for 30 minutes after each process. The prepared TiO₂ electrode was immersed in each dye solution and left for 24 hours in the dark to allow the dye to attach to the TiO₂ surface. The TiO₂/dye electrode was washed in ethanol and dried before assembling the DSSC. The counter electrode was prepared by spin coating a thin layer of platinum (Pt) solution (*chloroplatinic acid* diluted to 0.005 M in 2-propanol) on the conducting surface of a cleaned ITO glass and sintered at 450°C for 30 minutes [21]. In this study, DSSCs were illuminated from the Pt counter electrode side. Hence the prepared Pt counter electrode should be highly transparent.

2.5. Preparation of DSSCs. The DSSCs were prepared using a photoelectrode with 0.16 cm² working area, a counter electrode of Pt-coated ITO glass, and an electrolyte film containing (PVDF-HFP), KI, a mixture of EC/PC plasticizer, and a small amount of iodine. The DSSCs were fabricated by sandwiching the electrolyte between the TiO₂ and Pt electrodes.

2.6. Characterization and Measurements. For the polymer electrolytes, electrochemical impedance spectroscopy (EIS) technique was used to determine the highest conducting composition. The impedance of the samples was measured using the HIOKI 3520 LCR Hi-Tester interfaced to a computer with frequency ranging from 50 Hz to 100 kHz at room temperature. Each sample was sandwiched between two stainless steel electrodes of diameter 2.0 cm before performing the measurement. The conductivity was calculated using equation

$$\sigma = \frac{l}{R_B A}. \quad (1)$$

Here R_B is the bulk resistance taken at the intersection of the Nyquist plot with the real impedance axis, l is the film thickness, and A is the surface area of the electrode/electrolyte contact. The absorption spectrum of the different dyes was taken with Shimadzu UV-1650PC UV-vis spectrophotometer. The photocurrent-voltage ($I-V$) characteristics of the DSSCs were measured under illumination from a xenon lamp at the intensity of 100 Mw cm⁻² using a Keithley 2400 electro meter. The fill factor (FF) was calculated using the equation

$$FF = \frac{I_{\max} V_{\max}}{I_{\text{SC}} V_{\text{OC}}}, \quad (2)$$

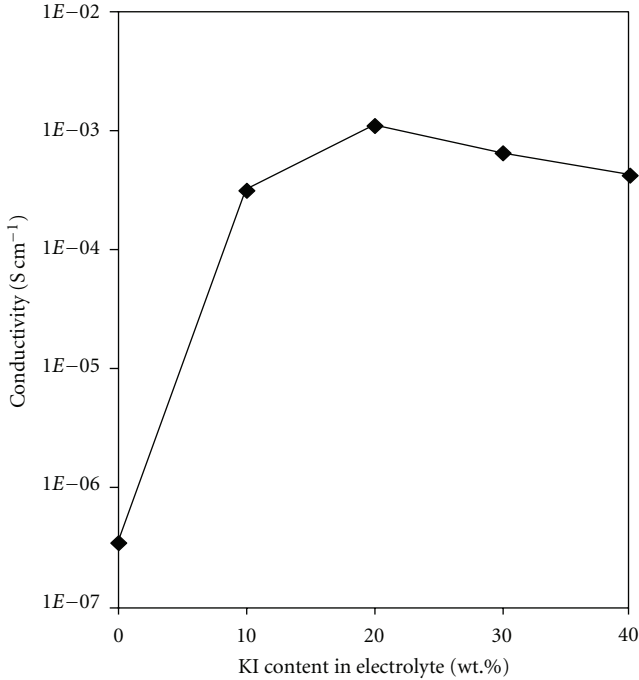


FIGURE 1: Conductivity of PVDF-HFP electrolyte with different salt contents.

where I_{\max} and V_{\max} are the maximum output value of current and voltage, respectively, and I_{SC} and V_{OC} are the short-circuit current and open-circuit voltage, respectively. The total energy conversion efficiency was calculated using the equation

$$\eta = \frac{I_{\text{SC}} V_{\text{OC}} \times \text{FF}}{P_{\text{in}}}, \quad (3)$$

where P_{in} is the power of incident light.

3. Results and Discussion

3.1. EIS of Polymer Electrolytes. The plot of room temperature conductivity of the electrolyte as a function of salt content is shown in Figure 1. The conductivity increases with the salt concentration, reaching a maximum value of $1.10 \times 10^{-3} \text{ S cm}^{-1}$ at 20 wt. % salt and gradually decreases thereafter. Conductivity increase is due to the increase of charge carriers or mobile ions when the salt content was increased. At high salt concentration, the distance between dissociated ions may become too close to each other enabling them to recombine into neutral ion-pairs which do not contribute to conductivity. Such phenomenon has been reported in the literature [22–24] and can be proven through Fourier transform impedance spectroscopy. The use of 50 wt. % EC/PC as plasticizers in the electrolyte helps to promote ion transfer and ion dissociation that enhances the conductivity. It is reported that the addition of plasticizers (up to 50 wt.%) enhances conductivity without compromising thermal, electrochemical, and dimensional stability of the electrolyte and the most employed plasticizers are low-molecular-weight

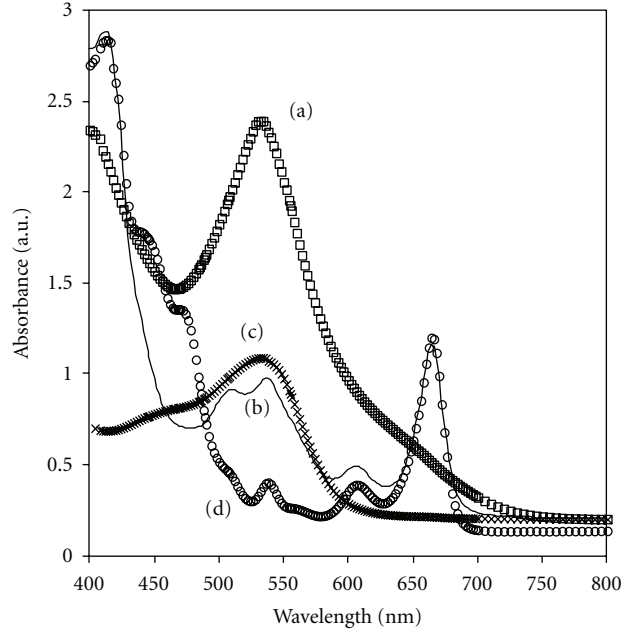


FIGURE 2: Absorption spectra of different dye materials. (a) Ruthenizer 535 (N3), (b) anthocyanin/chlorophyll mixture, (c) anthocyanin, (d) chlorophyll.

organic solvents such as propylene carbonate (PC) and ethylene carbonate (EC) [25, 26].

3.2. Characterizations of Natural Dye Sensitizers. Figure 2 shows the absorption spectra of Ruthenizer 535 (N3), anthocyanin, chlorophyll and a mixture of anthocyanin and chlorophyll, sensitizers at 1:1 volume ratio. The N3 dye exhibits maximum absorption at 535 nm, anthocyanin from black rice extraction at 532 nm, chlorophyll at 413 and 665 nm, and the mixture of black-rice and chlorophyll shows maximum peaks at 413, 536, and 665 nm. Since the sun's spectrum peaks at 550 nm, N3 and anthocyanin dyes should be able to absorb maximum sunlight and yield higher possibility of light harvesting [14]. Chlorophylls, which act as an effective photosensitizer in photosynthesis of green plant, has absorption maximum at 670 nm, thus, it is an attractive potential compound as a photosensitizer in the visible region [16]. It is also found that more absorption peaks are found when two natural dyes are mixed which shows that the absorption range is enhanced. This indicates the possibility of increasing the photoelectric conversion efficiency of a dye-sensitized solar cell with mixed dyes [27].

3.3. Characterizations of DSSCs. The photocurrent density-voltage graphs for DSSCs with different dyes material are shown in Figure 3. The values of open-circuit voltage (V_{OC}), short-circuit current density (I_{SC}), fill factor (FF), and conversion efficiency (η) obtained from Figure 3 are summarized in Table 2. Compared to the natural dye sensitizers, DSSC with Ruthenizer 535 (N3) dye shows the best overall performance with the short-circuit current density of 8.16 mA cm^{-2} , open-circuit voltage of 0.76 V, fill factor of

TABLE 2: The performance parameters of DSSCs with different dyes.

	N3	Anthocyanin	Chlorophyll	Anthocyanin + Chlorophyll
J_{sc} (mA cm^{-2})	8.16	3.02	1.61	3.26
V_{oc} (V)	0.76	0.36	0.36	0.36
FF	0.35	0.34	0.41	0.36
Efficiency (%)	2.17	0.37	0.24	0.42

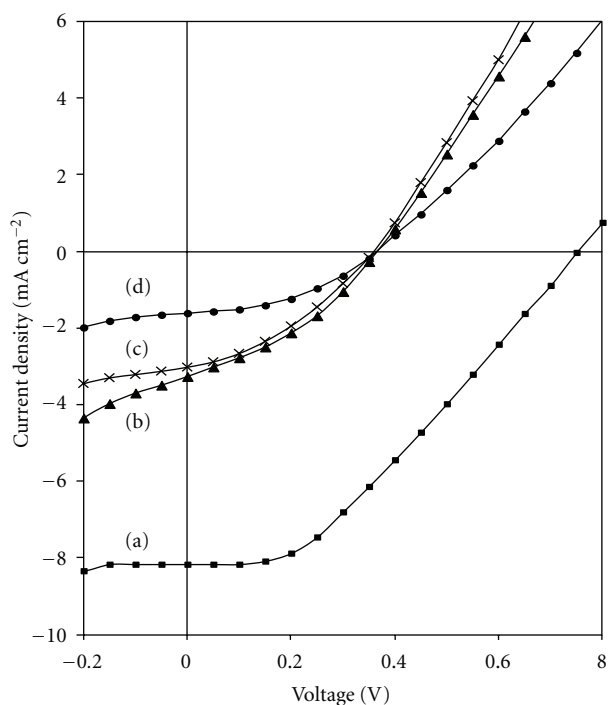


FIGURE 3: J - V curves for DSSCs with different dye materials. (a) Ruthenizer 535 (N3), (b) anthocyanin/chlorophyll mixture, (c) anthocyanin, (d) chlorophyll.

0.35, and photoconversion efficiency of 2.2%. For natural dyes, the mixed dye system shows better efficiency than dyes prepared using individual chlorophyll or anthocyanin extract. This suggests the possibility of utilizing multi-natural-dye mixture of different proportions and additives for the production of better absorbing dyes.

4. Conclusions

DSSCs have been fabricated using the highest conducting plasticized PVDF-HFP polymer electrolyte containing iodine/triiodide redox couple with N3, anthocyanin (from black rice extraction), and chlorophyll (from *pandan* extract) dyes as sensitizer. The DSSC using Ruthenizer 535 (N3) dye exhibits the best performance with a short-circuit current density of 8.16 mA cm^{-2} , open-circuit voltage of 0.76 V , fill factor of 0.35, and the highest photoconversion efficiency of 2.2%. As for the DSSC fabricated using natural dyes, the device with anthocyanin dye shows better performance compared to chlorophyll with a short-circuit current density of 1.07 mA cm^{-2} , open-circuit voltage 0.43 V , fill factor 0.33, and efficiency of 0.2% under the illumination of

100 mW cm^{-2} white light. However, the mixed dye system shows improved conversion efficiency suggesting that multi-dye mixtures may be more suitable for improving the efficiency of DSSCs.

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