



Effects of environmentally benign solvents in the agarose gel electrolytes on dye-sensitized solar cells

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ABSTRACT

The ionic agarose gel electrolytes are prepared by using environmental benign solvents and co-solvents to improve the agarose solubility and capacities of the additives for dye-sensitized solar cells. The effects of single solvents (dimethyl sulfoxide (DMSO), propylene carbonate (PC), propylene glycol, triethylene glycol, and tetraethylene glycol) and DMSO-based co-solvents are examined on the conductivities, diffusion coefficients of triiodide, and energy conversion efficiencies. The highest conductivity, 14.2 mS cm^{-1} , and the highest diffusion coefficient of triiodide, $2.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, are achieved for the electrolyte containing the co-solvent of 80 vol.% PC and 20 vol.% DMSO. The environmental benign co-solvent such as DMSO/PC can significantly increase the conversion efficiency to 3.4% with agarose compared to pure MPII with agarose (1.4%), while retaining $\sim 80\%$ of the energy conversion efficiencies of the reference cell without agarose under the illumination at AM 1.5, 100 mW cm^{-2} .

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted great attention since the major breakthrough in the conversion efficiency made by O'Regan and Grätzel [1]. A traditional DSSC is constructed by an electrode consisting of a porous TiO_2 layer with dye adsorbed on the TiO_2 surface, organic liquid electrolyte solution containing a I^-/I_3^- redox couple, and a platinum-coated counter electrode. Over the past two decades, DSSCs have been developed as solar cell candidates due to their low-cost, relatively high conversion efficiency, and higher efficiencies at higher temperatures [2].

The most efficient DSSC is reported to possess high conversion efficiency greater than 11% [3], which shows promise as a low-cost renewable energy source. However, electrolyte loss caused by leakage and volatilization of liquid electrolytes has been one of the major problems limiting the long-term use of DSSCs. In order to overcome this problem, solidifying liquid electrolyte forming gel or quasi-solid-state electrolytes has been the primary solution to make the sealing process easier and to minimize the loss of electrolytes for enhanced durability. Typically, polymers [4–7], low molecular weight gelators [8] and nanoparticles [9] are gelled with liquid electrolytes to form quasi-solid-state electrolytes. Quasi-solid-state DSSCs made by polyacrylonitrile (PAN) [4], poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF/HFP) [5], poly(ethylene oxide) (PEO) [6] and their copolymer [7] maintain over 90% of the efficiencies of DSSCs using liquid electrolytes.

Another approach uses natural materials such as polysaccharides to gel the liquid electrolytes of DSSCs, which prevents environmental pollution by not forming wastes requiring disposal or additional treatment. Agarose, a linear polymer of carbohydrates from seaweed, can act as the gelator of aqueous electrolytes and form a porous matrix when the hot solution with 0.5–5 wt.% agarose is cooled down. In recent years, agarose has been used as the matrix of the gel electrolyte for DSSCs. In general, there are two methods to obtain agarose gel electrolytes. One is to dissolve agarose in pure hot water, pour the solution on a FTO/ TiO_2 /dye electrode, and then soak the electrode in the solution containing a redox electrolyte to exchange water [10,11]. The other method is to dissolve agarose in ionic liquid directly [12,13]. The preparation of the former is complicated and the concentrations of the additives and water are hard to determine. In the latter method, the capacity of LiI in the ionic liquid was found to decrease, resulting in a 10% reduction in efficiency [12]. To make it worse, many additives such as LiI [14], 4-*tert*-butylpyridine (*t*-TBP) [15], 1-methylbenzimidazole (NMBI) [16] and guanidium thiocyanate (GuSCN) [17], are commonly used to improve the performance of DSSCs, which further decreases the capacities of ionic liquids. Thus, the low solubility of agarose in some ionic liquids and the decreased capacities of ionic liquids due to additives are the challenging issues for the use of polysaccharides. Therefore, this study attempts to choose appropriate solvents for agarose ionic gel to increase the amount of additives and improve the efficiency of DSSCs.

The requirements of solvents for ionic agarose gel for DSSCs include high boiling point, low vapor pressure, and compatibility with agarose. Solvents with low toxicity are also considered as an important prerequisite for our integral pursuit of environmentally

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benign chemistry as well as the use of non-polluting agarose. In this study, our objective is to reduce or eliminate the solvents and matrix in the gel electrolytes that are hazardous to human health or the environment. Specifically, the ionic gel electrolytes in this study consisted of 1-methyl-3-propylimidazolium iodide (MPII), effective solvents, and agarose. Single solvents and DMSO-based co-solvents with high boiling point, low vapor pressure, and low toxicity were studied for their capacities in the ionic agarose gel and their impacts on electrochemical properties and conversion efficiency for DSSCs. The electrochemical properties such as conductivity and diffusion coefficient of the ionic agarose gel with single solvents and co-solvents were studied by AC impedance and cyclic voltammetry. Moreover, the photoelectric conversion efficiencies of the DSSCs were measured. The role of the co-solvent in ionic agarose electrolytes for DSSCs are discussed and elucidated.

2. Experimental

2.1. Materials

1-Methylimidazole (97%), propyl iodide (98%), iodine (99.8%) and 4-*tert*-butylpyridine (96%) were purchased from Acros Organics. Agarose type VII, triethylene glycol (99%), tetraethylene glycol (99%), propylene glycol, propylene carbonate (99%), dimethyl sulfoxide (99.7%) were obtained from Sigma and guanidinium thiocyanate (99%) (GuSCN) and *N*-methylbenzimidazole (99%) (NMBI) were purchased from Alfa Aesar. N719 (ruthenium 535-bis TBA) was procured from UniRegion BioTech. All organic materials and TiO₂ (P25, Degussa AG) were used as-received without further purification.

2.2. Synthesis of 1-methyl-3-propylimidazolium iodide (MPII)

The synthesis procedure for MPII followed previously reported methodology [18]. 1-Methylimidazole and propyl iodide (molar ratio of 1:1.1) were first mixed in the vessel, and were then placed into an ultrasonic bath for 4 h. A yellow liquid was obtained and washed by acetone and ethyl acetate 3 times. After the solvents were removed by a rotary evaporator, the product was dried under a vacuum for 12 h at 50 °C. The yield of 1-methyl-3-propylimidazolium iodide was 93%. The MPII structure was validated by ¹H NMR spectroscopy and electrospray ionization mass spectroscopy.

2.3. Preparation of agarose gels

The solutions consisting of 1.8 M MPII, 5 wt% DI water, and 0.5 wt% agarose in various solvents were heated to 150 °C until the agarose was completely dissolved. Additives such as 0.1 M guanidinium thiocyanate (GuSCN), 0.5 M *N*-methylbenzimidazole (NMBI), and 0.1 M I₂ were then mixed into the hot agarose solutions. Gel electrolytes were obtained after the solutions were cooled down.

2.4. Measurement of the electrochemical properties of electrolytes

The sandwich type cell was fabricated by two platinum-coated ITO (indium-doped tin oxide) glasses as the electrodes with a gap of about 25 μm, which was sealed by the adhesive on the edge. Electrolytes were then injected into the cell through the gap. Steady-state current–voltage curve and conductivity (σ) were measured by using Solartron SI1287 and HP 4194A. The conductivity was calculated by the following Eq. (1):

$$\sigma = \frac{L}{AR_b} \quad (1)$$

Here L is the gap of symmetric cell and A is the area of the electrode. R_b is the bulk resistance of the gel electrolyte measured by impedance analyzer at 0.1 MHz. The limited current was determined in the voltage range between -0.8 V and 0.8 V at a scan rate of 5 mV s⁻¹. The diffusion coefficient of triiodide was calculated by the following Eq. (2):

$$D_{I_3^-} = \frac{I_{lim}d}{2nFC} \quad (2)$$

where $D_{I_3^-}$ is the diffusion constant of triiodide, I_{lim} is the limiting current density, d is the cell gap, n is the number of the electrons, F is the Faraday constant and C is the initial I₂ concentration.

2.5. Fabrication of a dye-sensitized solar cell

ITO-coated glass (7 Ω/square) was cleaned in acetone and ethanol using an ultrasonic cleaner prior to use. Commercial nanocrystalline TiO₂ (P25) and P123 [poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol)] were mixed in *n*-butanol to form TiO₂ colloidal suspension. A TiO₂ layer (~10 μm) was subsequently prepared by a doctor-blade coating technique onto the ITO/glass, which was then sintered at 400 °C for 1 h. The TiO₂/ITO/glass anode was immersed in a 0.1 M TiCl₄ aqueous solution for 30 min in an ice bath, and then sintered at 400 °C again to make a good binding between TiO₂ particles and at the interface between TiO₂ particles and the conducting glass. Finally, the ITO/TiO₂ photo-anode was sensitized in a N719 dye/ethanol solution (3×10^{-4} M) at room temperature for 24 h. DSSC was fabricated by sealing the dye-sensitized TiO₂ photo-anode and Pt-sputtered cathode around 100 °C with a 60 μm hot melt sealing foil (SX1170-60, SOLARONIX), which also served as a spacer. A DSSC cell (active area 0.25 cm²) was completed upon the injection of the electrolyte into the cell.

2.6. Photoelectrochemical measurement

An AM1.5 Solar Simulator (Newport 3A) was used as the light source with the incident light at 1 sun (100 mW cm⁻²) calibrated by a standard Si solar cell (ORIEL), to evaluate the photo-current conversion efficiency. I - V curves were measured by scanning the DSSCs from the short current condition (J_{sc}) to the open circuit voltage (V_{oc}) of the cell. The conversion efficiency of DSSC based on photocurrent vs. voltage (I - V) curve was recorded with a Keithley 2400 source meter. All measurements in this study were carried out at room temperature, 25 °C.

3. Results and discussion

3.1. Selection of environmentally benign solvents for agarose gel

Agarose is a polysaccharide extracted from seaweed with a repeating structure of 1,3-linked β-D-galactopyranose and 1,4-linked 3,6-anhydro-α-L-galactopyranose. The gelation mechanism of agarose has been reported as illustrated in Fig. 1 [19], in which double helices (Gel II) are formed from random coils in the solution via an intermediate state (Gel I) with mixed single and double helices upon cooling. However, the solubility of agarose in MPII is low and the capacity of additives in the agarose gel is scanty. In general, the addition of additives could restrain the dark current [15,16] and improve the photoelectric conversion efficiency. Therefore, appropriate solvents are required to increase the solubility of the commonly used additives such as LiI, 4-*tert*-butylpyridine (TBP), guanidinium thiocyanate (GuSCN), and *N*-methylbenzimidazole (NMBI) in the agarose gel. Typically, agarose can dissolve in

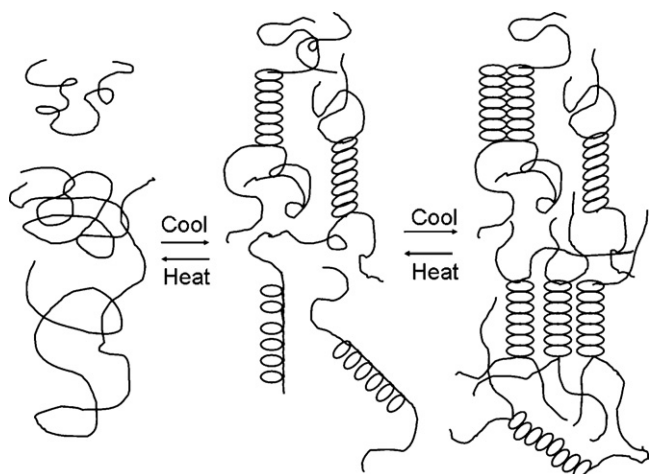


Fig. 1. Gelation mechanism of agarose: starting from random coils in the hot solution to mixed random coils, single and double helices in the intermediate stage (Gel I), then to the formation of double helices in the cool solution (Gel II). Adapted from Ref. [19].

dimethyl sulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMAc), and boiling water [20]. Among these solvents, LD₅₀, which is the dosage of chemical given all at once, causing the death of 50% of test animals, for DMF and DMAc are 2.8 and 5.1 g kg⁻¹, respectively. Such an LD₅₀ level is not benign to animals and human beings. Currently, many solvents and plasticizers such as acetonitrile (ACN) [21], 3-methoxypropionitrile (MPN) [22], and gamma-butyrolactone (GBL) [23] have been utilized in DSSCs for achieving high efficiencies. However, these solvents with LD₅₀ in the range of 1.5–4.0 g kg⁻¹ exhibit acute oral toxicity. ACN shows high performance in DSSCs, but exhibits toxicity to human organs [24]. Thus, low toxicity of solvents is considered as an important prerequisite in our effort to develop environmentally benign chemistry as well as the use of non-polluting agarose for DSSCs.

In this study, the LD₅₀ levels of the environmentally benign solvents were chosen to be higher than 14 g kg⁻¹. In addition, high boiling point and low vapor pressure were preferred. Specifically, DMSO, PC, propylene glycol (PG), triethylene glycol (3EG), and tetraethylene glycol (4EG) were selected. Table 1 summarizes their key properties, including boiling point, melting point, vapor pressure, viscosity, and dielectric constant. Common solvents, ACN and MPN, are also listed in Table 1 for the sake of comparison. The boiling points of these environmentally benign solvents are higher than 180 °C, while their vapor pressures are lower than 0.6 hPa at 20 °C. Such characteristics make these solvents (DMSO, PC, PG, 3EG, and 4EG) excellent candidates for DSSC devices.

3.2. Influence of the solvents on the diffusivity and photovoltaic performance

The choice of solvents for agarose was limited because of the poor solubility of agarose in most organic solvents. Among the

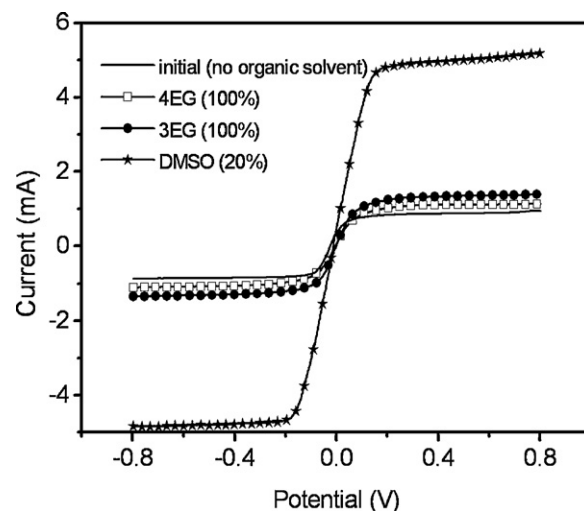


Fig. 2. Steady-state current–voltage curves of the gel electrolytes containing various solvents.

DMSO, 3EG, 4EG, PG and PC, DMSO is a good solvent for agarose, while 3EG, 4EG, PG, and PC are the poor solvents of agarose due to their poor solubility. In addition, agarose was found to precipitate when PC or PG was added in agarose/MPII hot solution. Agarose/MPII dissolved well after adding 3EG, 4EG, or DMSO. Also, when 3EG or 4EG was used as solvent, the ratio of MPII to 3EG or 4EG had to be higher than 3:10 (1.2 M in solvent) in order to dissolve agarose completely. As a result, the concentration of 1.8 M MPII was applied to all the agarose gel electrolytes in the subsequent sections because the highest efficiencies were revealed after comparing with 1.2 and 2.0 M in 3EG and 4EG.

The agarose gel electrolytes were then prepared using various solvents (DMSO, 3EG, and 4EG) at different concentrations. The solubility of agarose in DMSO was found to be much higher than that in 3EG or 4EG. Also, gelation did not occur when the amount of DMSO was more than 20 vol.% in the agarose gel electrolyte. It is believed that there is a strong interaction between agarose and DMSO [25], making the chains of agarose well extended in DMSO and thus hard to aggregate and form agarose with DMSO at >20 vol.%. The diffusion-limited currents of the agarose electrolytes with various solvents were measured by cyclic voltammetry using a symmetric thin layer electrochemical cell, as shown in Fig. 2. This showed that the diffusion limited currents for electrolytes based on DMSO were higher than those based on 100 vol.% for 3EG and 4EG. The diffusion coefficients of triiodide ions in the initial state (no organic solvent) for 3EG and 4EG systems were $6.1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $2.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $2.2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively. In contrast, a higher diffusion coefficient of $4.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ was achieved using an electrolyte containing only 20 vol.% DMSO.

The effect of the solvents (DMSO, 3EG and 4EG) on the performance of DSSCs was examined by the current density vs. voltage. The addition of the solvents in the weight percentage range of 0–100 improved not only the open circuit voltage (V_{oc}) but also the

Table 1
Key properties and LD₅₀ of common and selected solvents for the agarose gel electrolytes.

	DMSO	PC	PG	3EG	4EG	ACN	MPN
Melting point (°C)	18.4	−49	−59	−7	−6	−48	−50
Boiling point (°C)	189	242	188	285	314	82	165
Vapor pressure (hPa at 20 °C)	0.56	0.04	0.11	<0.001	<0.001	91.7	2.29
Viscosity (mPa s)	2	2.8	49	48	62	0.37	1.6
Dielectric constant	46.5	64.4	32	23.69	20.44	38	40
LD ₅₀ Orl-rat (g kg ⁻¹)	14	29	20	15–17	28–34	2.5	4.4

The values of the properties were acquired from the material safety data sheets from Sigma–Aldrich.

Table 2
Photovoltaic performances of DSSC based on gel electrolytes using different solvents.

Solvent	Initial	3EG		4EG		DMSO		
	vol.% of solvent	0	50	100	50	100	10	20
V_{oc} (V)	0.45	0.60	0.61	0.59	0.61	0.53	0.58	
J_{sc} (mA cm^{-2})	2.69	2.58	3.22	2.35	3.20	3.05	3.69	
FF	0.55	0.57	0.57	0.60	0.55	0.48	0.54	
η (%)	0.68	0.88	1.13	0.83	1.08	0.78	1.15	

short-circuit current density (J_{sc}), as summarized in Table 2. When 50% 3EG and 4EG solvents were added into the initial gel electrolyte (without organic solvent), their J_{sc} values (2.58 and 2.35 mA cm^{-2}) were smaller than that of the initial gel electrolyte (2.69 mA cm^{-2}). When more glycol up to 100 vol.% was added, J_{sc} was increased to 3.22 and 3.20 mA cm^{-2} for 3EG and 4EG, respectively, presumably due to a 260% increase in diffusion coefficient. V_{oc} was again increased as more glycol was added. The efficiency of the DSSCs increased with increasing concentrations of 3EG, 4EG, and DMSO as illustrated in Fig. 3. The efficiency of the DSSC was raised from 0.68% for the initial electrolyte (without organic solvent) to 1.15% for DMSO (at 20 vol.%), 1.13% for 3EG (at 100 vol.%), and 1.08% for 4EG (at 100 vol.%). In specific, DMSO (at ≤ 20 vol.%) exhibited much better performance than the initial electrolyte.

In order to expand our choice of solvents for agarose gel electrolytes and obtain a good balance between solubility and agarose gel, we mixed good and poor solvents in this study to improve the performance of the agarose gel electrolytes for the DSSCs. In the co-solvents, DMSO serves as a good solvent for agarose. For the mixture of good (DMSO) and poor solvents (3EG, 4EG, PC, or PG), we found that agarose cannot be completely dissolved if the volume ratio of good to poor solvent is lower than 1:9. On the other hand, when the volume ratio is higher than 3:7, the gelation of agarose cannot occur either. As a result, a volume ratio of 2:8 was employed for the subsequent sections in this paper. The diffusion-limited currents of the electrolytes containing various co-solvents (DMSO/3EG, DMSO/4EG, DMSO/PC, and DMSO/PG) were measured by cyclic voltammetry, as illustrated in Fig. 4. The diffusion-limited current for the electrolyte using DMSO/PC co-solvent was the highest. The current did not reach its diffusion limit up to 0.8 V as compared to 0.2 V for the other co-solvents. The I_3^- diffusion coefficient and conductivity of DMSO-based co-solvents, and their electric characteristics (V_{oc} , J_{sc} , and conversion efficiency) are summarized in Table 3. The highest ionic conductivity (14.2 mS cm^{-1}) and diffusion coefficient ($2.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)

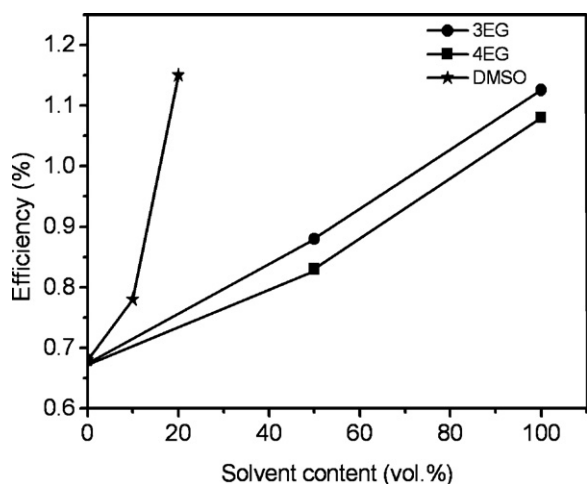


Fig. 3. The overall energy conversion efficiencies as a function of solvents and solvent content.

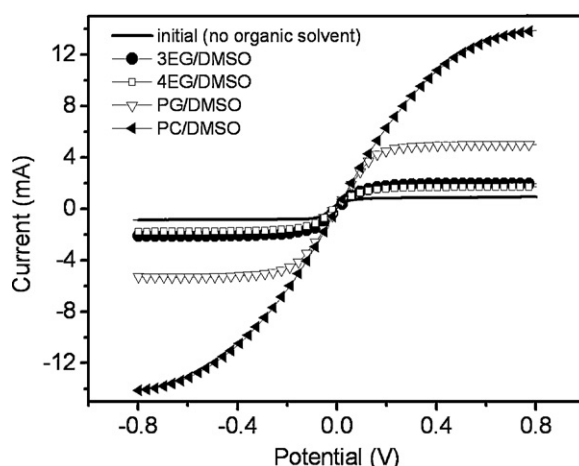


Fig. 4. Steady-state current–voltage curves of the gel electrolytes containing various DMSO co-solvents.

were observed in the gel electrolyte using a DMSO/PC co-solvent. In contrast, the lowest values of conductivity (4.4 mS cm^{-1}) and triiodide diffusion coefficient ($3.0 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) were found in the DMSO/4EG co-solvent. The conductivity and triiodide diffusion coefficient of the DMSO-based co-solvents decreased in the following order: PC > PG > 3EG > 4EG. The dielectric constants of these DMSO-based co-solvents showed the same trend, while their viscosities showed the opposite trend with the lowest viscosity for the DMSO/PC co-solvent. High dielectric constant and low viscosity of co-solvents like those of DMSO/PC presumably increase the dissociation of the solutes in the gel electrolytes and allow the ions to move faster in the agarose matrix, leading to high conductivity and high triiodide diffusivity. Fig. 5 shows the efficiencies of DSSCs with electrolytes containing various DMSO-based co-solvents. The photoelectric conversion efficiency was enhanced with the addition of organic solvents. The DSSC with DMSO/PC co-solvent in the agarose gel showed the highest V_{oc} , 0.73 V, highest J_{sc} , 4.65 mA cm^{-2} , and highest efficiency ($\eta = 1.97\%$), which was 62%, 73%, and 190% enhancement over the initial gel system (without organic solvent). The performance of PG/DMSO was the worst, yet its efficiency (1.06%) was still ~ 1.6 times higher than that of the initial gel system ($\eta = 0.68\%$). The efficiencies of DMSO-based co-solvents decreased in the following order: PC > 3EG \approx 4EG > PG. Furthermore, the efficiencies of electrolytes based on co-solvents

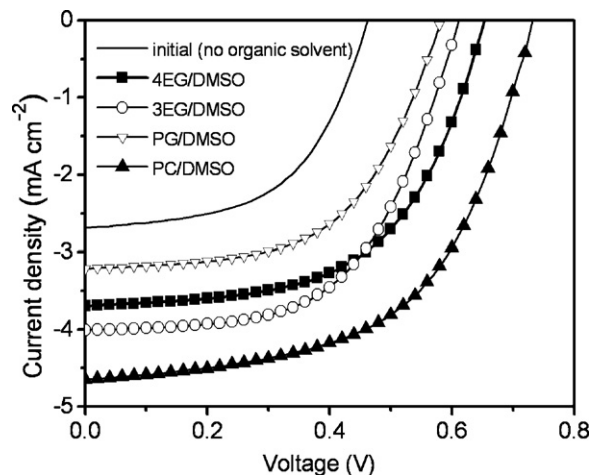


Fig. 5. J - V curves of DSSCs based on gel electrolytes using different DMSO co-solvents.

Table 3

Summary of the efficiencies, diffusion coefficients, conductivity, and DN of the gel electrolytes using different DMSO co-solvents.

Solvent	DMSO/PC	DMSO/4EG	DMSO/3EG	DMSO/PG	Pure DMSO (20 vol.%)
Conductivity (mS cm ⁻¹)	14.2	4.4	4.6	6.2	5.0
$D_{I_3^-}$ ($\times 10^{-7}$ cm ² s ⁻¹)	27.3	3.0	4.1	9.7	4.8
V_{oc} (V)	0.73	0.65	0.61	0.58	0.58
J_{sc} (mA cm ⁻²)	4.65	3.69	4.01	3.21	3.69
FF	0.58	0.57	0.57	0.57	0.54
η (%)	1.97	1.38	1.39	1.06	1.15

(excluding DMSO/PG) ($\eta = 1.38$ – 1.97%) are better than that using a single solvent, DMSO (at 20 vol.%) ($\eta = 1.15\%$).

When no organic solvent or only 20 wt.% DMSO was used, the I_3^- diffusion coefficients were low at 0.6×10^{-7} cm² s⁻¹ and 4.8×10^{-7} cm² s⁻¹, compared to 2.7×10^{-6} cm² s⁻¹ using DMSO/PC co-solvent. This implied that there was high I_3^- ion concentration around the TiO₂ nanoparticles in the DSSC. The higher I_3^- ion concentration might increase the charge recombination between the injected electrons and I_3^- at TiO₂/electrolyte interface.

As a result, the V_{oc} and J_{sc} were increased by the addition of organic solvents because the high I_3^- diffusion coefficient decreased the I_3^- ion concentration around the TiO₂, then reduced the dark current [26].

The diffusion limited current for the electrolyte and conductivity using DMSO/PG co-solvent was higher than those based on DMSO/3EG and DMSO/4EG co-solvents. Unexpectedly, the conversion efficiency of DSSC containing DMSO/PG was not higher than DMSO/3EG or DMSO/4EG. In order to elucidate the mechanism for the effect of different co-solvents on DSSCs performance, the desorbed dye levels in DMSO/PC, DMSO/3EG, DMSO/4EG, and DMSO/PG were then studied. This was carried out by immersing the dyed TiO₂ into the co-solvents for 1 h to collect the desorbed dye, whose amount was measured by the absorbance using a UV-vis spectrometer. The desorbed dye amount could be judged by the intensity of absorption peak around 310 nm. It was determined that more dyes were desorbed from TiO₂ when pure DMSO, 3EG, 4EG, and PC were added in the DMSO-based co-solvents as compared to PG. PG desorbed more dye from TiO₂ than PC, 4EG and 3EG. This was reason why the conversion efficiency of DSSC using DMSO/PG was lowest among these co-solvents.

So far, the best efficiencies remained low, for example, 0.68% for the reference cell using MPPII/agarose and 1.97% for the cell using the new electrolyte, MPPII/agarose with DMSO/PC co-solvent. Nevertheless, there are concerns about the low efficiencies and the merit of environmentally benign electrolytes. To address the concern of low efficiencies, we made a few changes in the cell fabrication, *i.e.* (1) replacing ITO glass by fluorine-doped tin oxide (FTO) ($8 \Omega/\text{square}$), (2) increasing the surface area in the TiO₂ layer by using a larger amount of polyethylene glycol (PEG) with higher surface area (surface area: $57.5 \text{ m}^2 \text{ g}^{-1}$), and (3) adding a $4 \mu\text{m}$ light scattering layer on $13 \mu\text{m}$ TiO₂ electrode. Higher conversion efficiencies were achieved after implementing afore-mentioned changes in the fabrication of the DSSCs. For instance, the efficiency of a reference cell using 3-methoxy-propionitrile (MPN)-based liquid electrolyte consisting of 0.5 M LiI, 0.05 M I₂, 0.1 M GuSCN and 0.2 M NMBI in MPN is 4.83%. As a result, we further use this improved cell to assess the merit of environmentally benign ion agarose electrolytes. When an environmental benign DMSO/PC co-solvent was used to replace MPN, the conversion efficiency was determined to be 4.63%. This showed environmentally benign DMSO/PC co-solvent offered comparable conversion efficiency with a mere $\sim 4\%$ reduction as compared to MPN solvent.

Subsequently, the impact of agarose on the conversion efficiency of DSSCs was evaluated. Because of the solubility issue, the additives for agarose gel electrolyte (1.8 M MPPII, 0.05 M I₂, 0.1 M GuSCN

and 0.5 M NMBI) were slightly different from MPN-based liquid electrolyte in the concentrations of MPPII and NMBI. When pure MPPII was used, the use of agarose reduced the efficiency $\sim 12\%$ from $\eta = 1.6\%$ to $\eta = 1.4\%$. While using slightly different additives, a conversion efficiency of $\eta = 4.3\%$ was obtained for DMSO/PC-based DSSC without agarose and 3.4% with agarose. A $\sim 21\%$ drop in efficiency to $\eta = 3.4\%$ was found when agarose was added. Therefore, the DSSC maintains about 80% of the conversion efficiency when 0.5 wt% agarose is added to the environmental benign DMSO/PC electrolyte.

4. Conclusions

The ionic agarose gel electrolytes have been prepared by using environmentally benign solvents and co-solvents to improve the agarose solubility and capacities of ionic liquids additives for the dye-sensitized solar cells. The highest conductivity, 14.2 mS cm^{-1} , and highest diffusion coefficient, $2.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, are achieved for the electrolyte containing the co-solvents with 80 vol.% PC and 20 vol.% DMSO. Such electrolyte yields a conversion efficiency of 3.4% based on improved cell fabrication, which is about 2.4 times higher than the electrolytes without organic solvents (pure MPPII with agarose, $\eta = 1.4\%$). The environmentally benign solvents with low viscosity and high dielectric constant increase the ionic conductivity and I_3^- diffusion coefficients, resulting in a reduction of the charge recombination between electrolyte and dye/TiO₂ interface and improved conversion efficiency.

The use of environmental benign solvents slightly reduces ($\sim 4\%$ drop) the conversion efficiency as compared to conventional solvent, MPN. However, the use of agarose reduces the conversion efficiency about 21% from $\eta = 4.3\%$ to $\eta = 3.4\%$ for DMSO/PC-based DSSC. Therefore, the DSSC maintains about 80% of the conversion efficiency when 0.5 wt% agarose is added to the environmental benign DMSO/PC electrolyte.

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