



# Dye-sensitized solar cells based on agarose gel electrolytes using allylimidazolium iodides and environmentally benign solvents

Hsin-Ling Hsu, Cheng-Fang Tien, Ya-Ting Yang, Jihperng Leu\*

Department of Materials Science and Engineering, National Chiao Tung University, 1001 University Road, Hsinchu 30010, Taiwan

## ARTICLE INFO

### Article history:

Received 15 October 2012

Accepted 30 December 2012

Available online 6 January 2013

### Keywords:

Allylimidazolium iodides

Ionic liquids

Agarose gel electrolyte

Dye-sensitized solar cell

Environmentally benign solvents

## ABSTRACT

Novel agarose gel electrolytes are prepared by allylimidazolium iodides-based ionic liquids and environmentally benign co-solvents (propylene carbonate (PC) and dimethyl sulfoxide (DMSO)) for dye-sensitized solar cells (DSSCs). Among 1-allyl-3-ethylimidazolium iodide (AEII), 1-allyl-3-propylimidazolium iodide (APII), 1-3-diallylimidazolium iodide (DAII), and 1-methyl-3-propylimidazolium iodide (MPII) ionic liquids, the agarose gel electrolyte containing AEII exhibits the best DSSC performance. The efficiency of the DSSC using the agarose gel electrolyte containing 1.5 M AEII and 0.65 wt% agarose is 5.89% with the highest  $I_3^-$  diffusion coefficient of  $7.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . The performance of the AEII ionic liquid-based agarose gel electrolyte is comparable to the liquid electrolyte based on 3-methoxypropionitrile (MPN) (5.84%) under illumination at AM 1.5,  $100 \text{ mW cm}^{-2}$ . Moreover, the DSSC performance of the allylimidazolium iodides ionic liquid-based agarose electrolyte is determined by the interaction between ionic liquid and agarose, which affects the rigidity of the ion channels and the  $I_3^-$  diffusion coefficient.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted great attention since the major breakthrough in conversion efficiency made by Grätzel and O'Regan [1]. Over the past two decades, DSSCs have become an attractive candidate for serving as a renewable energy source due to their low-cost, relatively high conversion efficiency, and higher efficiencies at higher temperatures. The most efficient DSSC has recently been reported to possess conversion efficiency greater than 12% [2]. A traditional DSSC is constructed by an electrode consisting of a porous  $\text{TiO}_2$  layer with dye adsorbed on the  $\text{TiO}_2$  surface, organic liquid electrolyte solution containing an  $I^-/I_3^-$  redox couple, and a platinum-coated counter electrode. Yet, liquid electrolyte loss caused by leakage and volatilization has been one of the major problems limiting the long-term use of DSSC. To overcome this problem, solidifying liquid electrolytes to form gel or quasi-solid-state electrolytes [3,4] and adding ionic liquids [5] are the viable solutions to make the sealing process easier and to minimize the loss of electrolytes for enhanced durability.

Ionic liquids have been widely used in lithium batteries [6], fuel cells [7], electric double-layer capacitors [8], electrochromic devices [9], and DSSC [10], because of their

non-flammability, negative vapor pressure, non-volatility, and high conductivity. In particular, allylimidazolium iodides, 1-methyl-3-propylimidazolium iodide (MPII), are commonly used as an ionic liquid in electrolytes [11,12]. In the electrolytes used for DSSC, the viscosity of the ionic liquid is critical in determining the ion transport and diffusion coefficients [13]. So far, most works have focused on the allylimidazolium iodides by modifying their substituent groups to tailor the properties, such as melting point, viscosity, conductivity, and thermal stability [14]. It has been reported that the viscosity of the imidazolium based ionic liquids can be reduced using asymmetric cations [11]. In addition, in certain cases, allyl groups attached to imidazolium cations have resulted in lower viscosity ionic liquids than 1, 3-dialkylimidazolium halides [15,16]. DSSCs using electrolytes based on supercooled allylimidazolium iodides, such as 1-allyl-3-methylimidazolium, AEII, and APII, have been found to provide good performance and stability [17].

Ionic liquids also possess good solubility of polysaccharides and biomacromolecules such as agarose, which are insoluble in most conventional organic solvents [18–20]. In our previous study, the agarose gel electrolytes were composed of MPII and the environmentally benign co-solvents, PC and DMSO, to improve the agarose solubility and capacities of ionic liquid additives for dye-sensitized solar cells [21]. In specific, DMSO was labeled as an environmentally friendly solvent, due to its low toxic potential [22]. Thus, in this study, we are motivated to further improve the solubility of the agarose gel electrolyte by adding ionic liquids. In addition, we plan to incorporate allyl group(s) onto the imidazolium cation in

\* Corresponding author. Tel.: +886 3 5131420; fax: +886 3 5724727.

E-mail address: [jimleu@mail.nctu.edu.tw](mailto:jimleu@mail.nctu.edu.tw) (J. Leu).

order to see if the viscosity of the resulting ionic liquids could be further reduced and to understand its impact on DSSC efficiency.

In this study, AEII, APII, and DAII were synthesized and introduced into the agarose gel electrolytes, to compare with a reference electrolyte based on the allylimidazolium iodide ionic liquid, MPII. The viscosities and diffusion coefficients of these ionic liquids and the ionic agarose gels were measured by rheometer and cyclic voltammetry, respectively. Moreover, the photoelectric conversion efficiencies and electrochemical properties of the DSSCs containing allylimidazolium iodides and MPII were characterized. The interaction between allylimidazolium iodides and agarose, the effects of the agarose content, and their impact on DSSC efficiency are examined and discussed.

## 2. Experimental

### 2.1. Materials

1-Methylimidazole (97%) and iodine (99.8%) were purchased from Acros Organics. Agarose type VII, propylene carbonate (99%) and dimethyl sulfoxide (99.7%) were obtained from Sigma and guanidinium thiocyanate (99%) (GuSCN), 1-allylimidazole (99%), iodoethane (98%), 1-iodopropane (98%), allyl iodide (97%) and N-methylbenzimidazole (99%) (NMBI) were purchased from Alfa Aesar. N719 (Ruthenium 535-bis TBA) was procured from UniRegion BioTech. The ethyl acetate (99.8%; HPLC grade) was obtained from ECHO. All organic materials 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 [21,23]. The synthesis reactions were carried out in water bath under sonication conditions for 4 h. For our work, an ultrasonic cleaner (Delta DC200; Delta New Instrument Co. Ltd., Taiwan) with 200 W power and 40 kHz frequency was used. The temperature of the synthesis was not specifically controlled and may be increased to 40 °C under sonication condition. The yield of 1-methyl-3-propylimidazolium iodide was 95%. The MPII structure was validated by <sup>1</sup>H NMR spectroscopy and electrospray ionization mass spectroscopy.

AEII, APII, and DAII were synthesized by the same procedure, while the ethyl acetate solvent was used and mixed with the starting materials in the synthesis of AEII and DAII.

### 2.3. Preparation of agarose gels

The solutions consisting of 1.5 M ionic liquid and agarose at different concentrations (0–1.0 wt%) in PC/DMSO co-solvents (volume ratio, 8:2) were heated to 150 °C until the agarose was completely dissolved. Additives such as 0.1 M guanidinium thiocyanate (GuSCN), 0.2 M N-methylbenzimidazole (NMBI), and 0.05 M I<sub>2</sub> were then mixed into the hot agarose solutions. Gel electrolytes were obtained after the solutions were cooled down.

### 2.4. Rheological measurements

All rheological data were collected using an AR-G2 stress-controlled rheometer (TA Instruments). The viscosity of the ionic liquids and agarose gels were measured in a temperature range from 25 to 150 °C (ramp rate: 5 °C/min.) and at an angular velocity of 0.1 rad/s. Agarose gels were compressed between two heated parallel plates with a gap of 0.5 mm.

### 2.5. 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 60 μm. The gap was sealed by the adhesive on the edge. Steady-state current-voltage curve was measured by using Solartron SI1287. 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<sup>-1</sup>. The diffusion coefficient of triiodide (D<sub>I<sub>3</sub><sup>-</sup></sub>) was calculated by Eq. (1):

$$D_{I_3^-} = \frac{I_{\text{lim}} d}{2nFC} \quad (1)$$

where  $I_{\text{lim}}$  is the limiting current density,  $d$  is the cell gap,  $n$  is the number of electrons,  $F$  is the Faraday constant, and  $C$  is the initial I<sub>2</sub> concentration.

### 2.6. Fabrication of a dye-sensitized solar cell

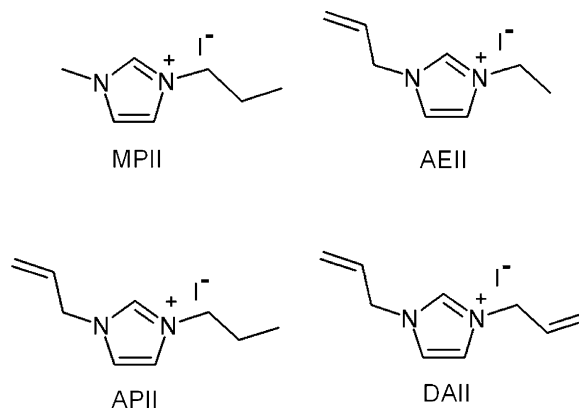
A double-layer TiO<sub>2</sub> was coated on fluorine-doped SnO<sub>2</sub> (FTO) conducting glass electrode by screen-printing. A 13 μm-thick TiO<sub>2</sub> film consisting of anatase TiO<sub>2</sub> (particle size: 20 nm) acted as the photoelectrode, while a 4 μm-thick TiO<sub>2</sub> film of 400 nm anatase TiO<sub>2</sub> served as the light-scattering layer. The details of the preparation of TiO<sub>2</sub> paste for screen-printing have been reported elsewhere [24]. Finally, the FTO/TiO<sub>2</sub> photo-anode was annealed at 500 °C for 15 min and then sensitized in an N719 dye/ethanol solution (5 × 10<sup>-4</sup> M) at room temperature for 24 h. DSSC was fabricated by sealing the dye-sensitized TiO<sub>2</sub> photo-anode and Pt-sputtered cathode around 100 °C with a 25 μm hot melt sealing foil (SX1170-60, Solaronix). A DSSC cell (active area 0.283 cm<sup>2</sup>) was completed upon the injection of the electrolyte into the cell.

### 2.7. Photoelectrochemical measurement

An AM1.5 Solar Simulator (Newport 3A) was used as the light source with the incident light at set at 1 Sun (100 mW cm<sup>-2</sup>) as calibrated by a standard Si solar cell (ORIEL) to evaluate the photocurrent conversion efficiency. 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

The chemical structures of AEII, APII, DAII and MPII as illustrated in Scheme 1.



**Scheme 1.** Molecular structures of MPII and allylimidazolium iodides (AEII, APII, and DAII).

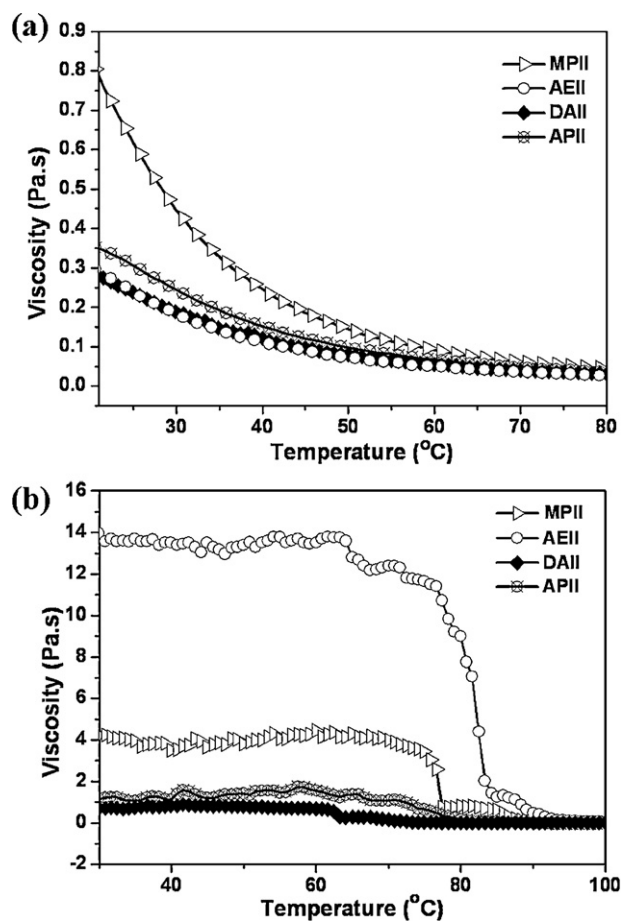


Fig. 1. (a) Dynamic viscosity as function of temperature for MPII, AEII, APII, and DAI ionic liquids and (b) dynamic viscosity as function of temperature for the agarose gels with MPII, AEII, APII, and DAI ionic liquids.

### 3.1. The viscosities of the ionic liquids and ionic agarose gels

The viscosity of the ionic liquid is an important mass transport property in an electrolyte. The temperature dependency of the dynamic viscosity of AEII, APII, DAI, and MPII ionic liquids were first measured and shown in Fig. 1(a). The viscosity at the same temperature ( $T \leq 70^\circ\text{C}$ ) decreased in the following order: MPII > APII > DAI  $\approx$  AEII. Moreover, the temperature dependency of AEII's dynamic viscosity was about the same as that of DAI. The viscosities of the three allylimidazolium iodides in this study were all lower than MPII, the conventional ionic liquid. Their viscosities were reduced dramatically because the allyl groups inhibited crystallization [17]. In addition, a decrease in alkyl chain length on the imidazolium cation was found to reduce the ionic liquid viscosity, as evidenced by the finding that the viscosity of AEII is lower than APII.

Next, the temperature-dependent dynamic viscosities of the agarose gels consisting of the ionic liquids and 0.5 wt% agarose in PC/DMSO co-solvents, are shown in Fig. 1(b). The agarose gel with AEII exhibited the highest viscosity, while the gel with DAI showed the lowest viscosity. Although AEII and DAI both exhibited low viscosity among the ionic liquids in Fig. 1(a), the notable difference in agarose gels viscosity indicated that the interaction between the ionic liquids and agarose plays a critical role in determining the viscosity of agarose gel. Different from most conventional organic solvents, ionic liquids can dissolve agarose by disrupting the hydrogen bonding within [25] to form hydrogen-bondings between the hydroxyl groups of agarose and the ionic liquids. In addition, both

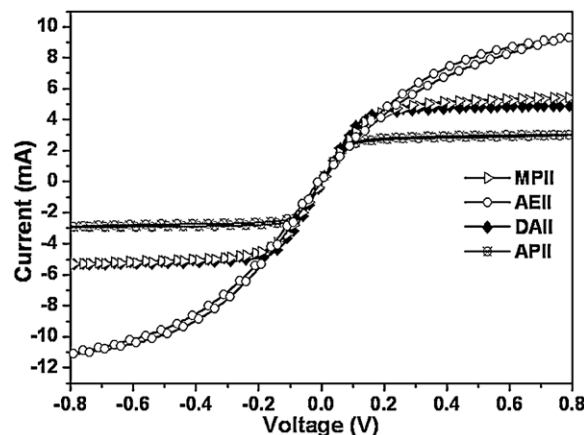


Fig. 2. Steady-state current–voltage curves of the gel electrolytes containing different ionic liquids.

the cation and anion of the ionic liquid can affect the solubility of agarose [18].

We then look into the gelation mechanism of agarose in the co-solvents system. Double helices are formed from random coils in the solution through an intermediate state with mixed single and double helices upon cooling [26]. More specifically, phase separation occurs when the solvent-rich region and the polymer-rich region, *i.e.* agarose gel appear after hot agarose solution is cooled down in the co-solvents system [21]. Similarly, the gelation of agarose solution involves conversion from disordered coils to ordered helix conformation, leading to different ion channels in the agarose gels for transporting the redox couples, depending on the interaction between the ionic liquid and the agarose. For APII and DAI, their larger imidazolium cations may inhibit the formation of helix and double helices [25]. In addition, the interaction between diallyl groups on the imidazolium ion of DAI and hydroxyl groups on agarose may further hinder the formation of helix and double helices. Both factors of DAI give rise to the weakest agarose gel as shown. In this case, large void space was created by fiber-like agarose consisting of more disordered agarose chains and less helices in the DAI system. In contrast, AEII has a smaller imidazolium cation and relatively weaker interaction with agarose due to its single allyl group and an alkyl side group. As a result, more ordered helix conformation was formed, leading to a stronger agarose based on AEII ionic liquid.

### 3.2. The performance of DSSCs with different allylimidazolium iodides

The diffusion-limited currents of the agarose electrolytes with various ionic liquids are shown in Fig. 2. The  $I_3^-$  diffusion coefficients are obtained from Eq. (1). The diffusion limited current and diffusion coefficient for the agarose electrolyte based on AEII was the highest among MPII, AEII, APII and DAI. The diffusion coefficients of agarose gel electrolytes for MPII, AEII, APII, and DAI ionic liquids were  $1.6 \times 10^{-6}$ ,  $5.6 \times 10^{-6}$ ,  $2.3 \times 10^{-6}$ , and  $1.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , respectively.

The effect of various ionic liquids (MPII, AEII, APII, and DAI) in the agarose gel electrolyte on the performance of DSSCs was further examined by the current density vs. voltage. The diffusion coefficients of the electrolytes, open circuit voltage ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), fill factor, and efficiencies of the DSSCs containing allylimidazolium iodides-based agarose gel electrolytes are summarized in Table 1, in which the DSSC cell containing the MPII-based agarose gel electrolyte was used as a reference. When 0.5 wt% agarose was dissolved in the mixtures of PC/DMSO, MPII

**Table 1**

Photovoltaic performances of DSSC based on gel electrolytes containing 0.5 wt% agarose and different ionic liquids and the diffusion coefficient of the electrolytes.

Ionic liquid	MPII <sup>a</sup>	MPII	AEII	APII	DAII
$D_{I_3^-}$ ( $\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ )	1.6	2.8	5.8	2.3	1.8
$V_{oc}$ (V)	0.63	0.70	0.72	0.70	0.70
$J_{sc}$ ( $\text{mA cm}^{-2}$ )	12.21	11.73	11.71	11.53	11.84
FF	0.61	0.64	0.65	0.62	0.60
$\eta$ (%)	4.72	5.25	5.45	4.97	4.96

<sup>a</sup> The liquid phase electrolyte without agarose.

and the additives, the efficiency was enhanced 11% from 4.72% to 5.25%. The  $V_{oc}$  was improved from 0.63 V to 0.70 V with the addition of agarose. Among four ionic liquids, the best efficiency was achieved by using the AEII agarose gel electrolyte. The AEII system delivered the highest  $V_{oc}$  (0.72 V) and FF (0.65), and relatively high  $J_{sc}$  ( $11.71 \text{ mA cm}^{-2}$ ), which was comparable to those of MPII, APII and DAII (11.73, 11.53, and  $11.84 \text{ mA cm}^{-2}$ ). Because of the more ordered helix and double-helices conformation and relatively weaker interaction between AEII and agarose, the  $I_3^-$  diffusion coefficient was enhanced through the rigid and stable ion channels and the concentration of  $I_3^-$  around  $\text{TiO}_2$  was reduced. Moreover, the dark reaction occurring from the electrons at  $\text{TiO}_2$  and  $I_3^-$  was reduced, resulting in an increased  $V_{oc}$ .

In contrast, the DSSC using the DAII agarose gel electrolyte showed the lowest open-circuit photovoltage ( $V_{oc}$ ), fill factor (FF), and photoelectric conversion efficiency among the allylimidazolium iodides, *i.e.* 0.70 V, 0.65, and 4.96%, respectively. These correlated well with the lowest  $I_3^-$  diffusion coefficient ( $1.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) in the DAII agarose gel electrolyte due to less ordered helix conformation, large void space in the agarose gel, and stronger interaction between the two allyl groups on the imidazolium cation and the agarose [27]. The lowest  $I_3^-$  diffusion coefficient of the DAII-based agarose electrolyte resulted in higher recombination, leading to the lowest efficiency and FF value. Regarding the high-viscosity APII ionic liquid, the DSSC using APII-based agarose gel electrolyte showed similar efficiency to that using DAII because of its comparably low agarose viscosity (Fig. 1b) resulting from a longer alkyl chain on imidazolium cation.

### 3.3. The effect of agarose concentration in the AEII system

The agarose gel electrolyte containing AEII (0.5 wt% agarose), demonstrated the best performance, indicating that both the viscosity of the ionic liquid and the interaction between ionic liquid and agarose are critical factors. Thus, we further examine the effect of agarose concentration on the DSSC cell performance using the AEII-based agarose gel electrolyte. Fig. 3 shows the  $I_3^-$  diffusion-limited currents of the agarose electrolytes with AEII ionic liquid containing various agarose concentrations, as measured by cyclic voltammetry using a symmetric thin layer electrochemical cell. The diffusion-limited current increased with increasing agarose content from 0 wt% to 0.65 wt%, and then decreased to a concentration >0.65 wt%. The  $I_3^-$  diffusion coefficients were  $2.3 \times 10^{-6}$ ,  $5.8 \times 10^{-6}$ ,  $7.7 \times 10^{-6}$ ,  $6.2 \times 10^{-6}$ , and  $1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  for 0 (liquid-phase electrolyte), 0.5, 0.65, 0.85, and 1.0 wt% agarose, respectively. The highest  $I_3^-$  diffusion coefficient ( $7.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) was found at the concentration of 0.65 wt%, while the lowest  $I_3^-$  diffusion coefficient ( $1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) was for the electrolyte with 1.0 wt% agarose.

Agarose is readily dissolved in AEII ionic liquid and is an environmentally benign PC/DMSO co-solvent for forming three-dimensional ion channels. With increasing agarose content up to 0.65 wt%, the rigidity and stability of ion channels in AEII and PC/DMSO-based agarose system were improved, resulting in a higher  $I_3^-$  diffusion coefficient. Above the optimal agarose

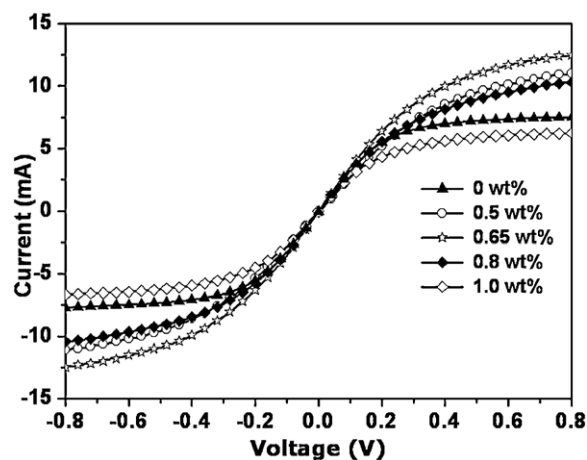


Fig. 3. Steady-state current–voltage curves of the gel electrolytes containing different concentrations of agarose.

concentration, the void space of the ion channels is reduced, leading to a lower  $I_3^-$  diffusion coefficient [28].

Under a  $100 \text{ mW cm}^{-2}$  light source, the  $I$ – $V$  curves and dark  $I$ – $V$  curves of the DSSCs containing AEII ionic liquid are illustrated in Fig. 4(a) and (b), respectively. The diffusion coefficients of the electrolytes,  $V_{oc}$ ,  $J_{sc}$ , fill factor, and the efficiencies of the DSSCs containing AEII-based agarose gel electrolytes at various agarose concentrations are summarized in Table 2. The electrolyte without agarose gel (0 wt%) exhibited the highest  $J_{sc}$ , but the lowest  $V_{oc}$ , FF, and efficiency. The efficiency increased as we increased the

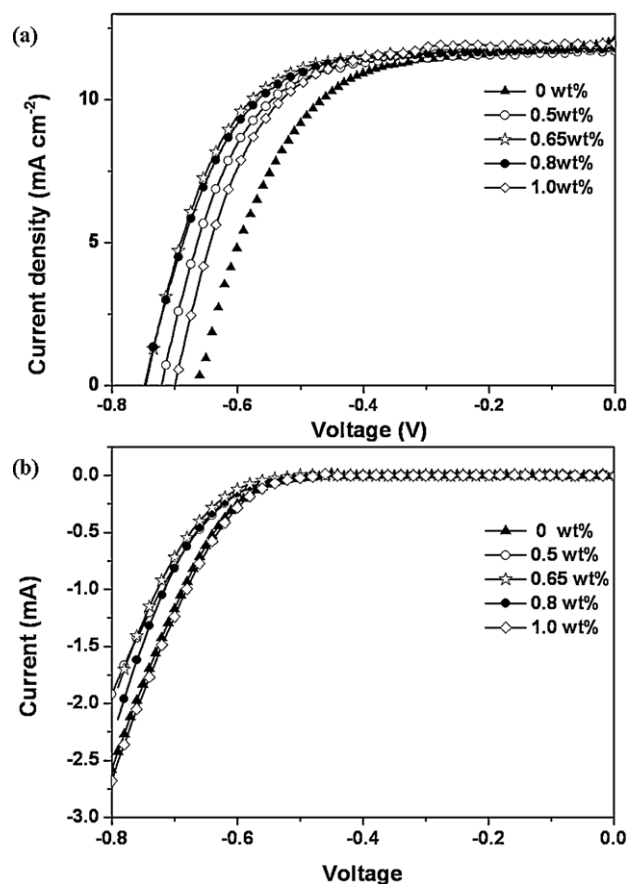


Fig. 4. (a) Light and (b) dark  $J$ – $V$  curves of DSSCs using AEII-based agarose gel electrolytes with various concentrations of agarose.



**Table 2**  
Photovoltaic performances of DSSC based on gel electrolytes with various concentrations and the diffusion coefficient of the electrolytes.

Agarose content	0 wt%	0.5 wt%	0.65 wt%	0.8 wt%	1.0 wt%
$D_{I_3^-}$ ( $\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ )	2.3	5.8	7.7	6.2	1.9
$V_{oc}$ (V)	0.66	0.72	0.76	0.75	0.70
$J_{sc}$ ( $\text{mA cm}^{-2}$ )	12.62	11.71	11.45	11.82	11.96
FF	0.60	0.65	0.68	0.64	0.63
$\eta$ (%)	4.97	5.45	5.89	5.68	5.31

amount of agarose up to 0.65 wt%, and then dropped as the amount of agarose was raised to 0.8 wt% and 1.0 wt%. The enhancement of efficiency relative to a no agarose case (0 wt%) is 9.7%, 18.5%, 14.2%, and 6.8% for agarose concentrations at 0.5, 0.65, 0.8 and 1 wt%, respectively. An increase of agarose concentration (up to 0.65 wt%) was accompanied by increasing  $V_{oc}$  and FF. The increased  $V_{oc}$  may result from the suppressed reduction in the back electrons transfer from the conducting band of  $\text{TiO}_2$  to the  $I_3^-$  in the electrolyte [29].

As summarized in Table 2, AEII-based agarose gel electrolytes yielded the highest triiodide diffusion coefficients at the optimal concentration of agarose (0.65 wt%). This lowered the concentration of  $I_3^-$  around the dyed  $\text{TiO}_2$  and reduced the recombination of oxidative dye and  $I_3^-$ . The injection of electrons from  $\text{TiO}_2$  was accelerated and the electron concentration on  $\text{TiO}_2$  was increased. Moreover, steric hindrance effect occurred as agarose adsorbed on  $\text{TiO}_2$ , which reduced the reaction between oxidative dye and  $I_3^-$ . The reduced recombination led to an increase in  $V_{oc}$  and FF. Overall, the best performance of the agarose gel electrolyte was 5.89% for 0.65 wt% agarose, which correlated with the highest triiodide diffusion coefficient ( $7.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ). In comparison, the conversion efficiency was 5.84% for the DSSC cell using an MPN-based liquid electrolyte containing 0.5 M LiI, 0.2 M NMBI, 0.1 M GuSCN and 0.05 M  $I_2$  in MPN. Thus, the AEII ionic liquid-based agarose gel electrolyte demonstrated comparable DSSC performance to the one using MPN-based liquid electrolyte.

#### 4. Conclusions

Low-viscosity ionic liquids, allylimidazolium iodides, were introduced to environmentally benign co-solvents (PC/DMSO) based agarose gel electrolytes for the fabrication of DSSCs. Among MPII, AEII, APII and DAII, the agarose gel electrolyte containing AEII exhibited the best DSSC performance. To be more specific, the efficiency of the DSSC using the agarose gel electrolyte containing 1.5 M AEII, 0.65 wt% agarose, 0.1 M GuSCN, 0.2 M NMBI, and 0.05 M  $I_2$  was 5.89% with an  $I_3^-$  diffusion coefficient of  $7.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . Even though the environmentally benign solvent and the natural product, agarose, were adapted in the electrolytes, the conversion efficiency ( $\eta = 5.89\%$ ) of the DSSC containing the agarose gel electrolyte based PC/DMSO and AEII was comparable with the liquid electrolyte based on MPN ( $\eta = 5.84\%$ ).

In summary, the DSSC performance of the allylimidazolium iodides ionic liquid-based agarose electrolyte was determined by the interaction between ionic liquid and agarose, which affects the rigidity of ion channels and the  $I_3^-$  diffusion coefficient. Even though AEII and DAII exhibited similar viscosity, their DSSC performance was quite different (5.45% vs. 4.96%). AEII had a smaller imidazolium cation and relatively weaker interaction with agarose due to its single allyl group and an alkyl side group. AEII possessed low-viscosity ionic liquid and high solubility agarose to form a low-viscosity agarose gel electrolyte. More ordered agarose helix and double helices were formed with rigid and stable ion channels in the agarose gel electrolyte, leading to the release of more ionic

liquid into the solvent with high diffusivity in the electrolyte and enhanced DSSC performance.

#### Acknowledgements

The authors thank the National Science Council of Taiwan for the financial support under grant nos: NSC 101-3113-E-007-001- and NSC101-2112-M-009-016-MY2.

#### References

- [1] M. Grätzel, B. O'Regan, A low-cost, high-efficiency solar cell based on dye-sensitized colloidal  $\text{TiO}_2$  films, *Nature* 353 (1991) 737.
- [2] A. Yella, H.-W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.-G. Diao, C.-Y. Yeh, S.M. Zakeeruddin, M. Grätzel, Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency, *Science* 334 (2011) 629.
- [3] J.E. Benedetto, A.D. Gonçalves, A.L.B. Formiga, M.A. De Paoli, X. Li, J.R. Durrant, A.F. Nogueira, A polymer gel electrolyte composed of a poly(ethylene oxide) copolymer and the influence of its composition on the dynamics and performance of dye-sensitized solar cells, *Journal of Power Sources* 195 (2010) 1246.
- [4] T.M.W.J. Bandara, M.A.K.L. Dissanayake, B.E. Mellander, Dye sensitized solar cells with poly(acrylonitrile) based plasticized electrolyte containing  $\text{MgI}_2$ , *Electrochimica Acta* 55 (2010) 2044.
- [5] D. Kuang, P. Wang, S. Ito, S.M. Zakeeruddin, M. Grätzel, Stable mesoscopic dye-sensitized solar cells based on tetracyanoborate ionic liquid electrolyte, *Journal of the American Chemical Society* 128 (2006) 7732.
- [6] L. Niedzicki, G.Z. Żukowska, M. Bukowska, P. Szczeciński, S. Grugeon, S. Laruelle, M. Armand, S. Panero, B. Scrosati, M. Marcinek, W. Wieczorek, New type of imidazole based salts designed specifically for lithium ion batteries, *Electrochimica Acta* 55 (2010) 1450.
- [7] R.F. de Souza, J.C. Padilha, R.S. Gonçalves, J. Dupont, Room temperature dialkylimidazolium ionic liquid-based fuel cells, *Electrochemistry Communications* 5 (2003) 728.
- [8] A. Orita, K. Kamijima, M. Yoshida, Allyl-functionalized ionic liquids as electrolytes for electric double-layer capacitors, *Journal of Power Sources* 195 (2010) 7471.
- [9] R. Marcilla, F. Alcaide, H. Sardon, J.A. Pomposo, C. Pozo-Gonzalo, D. Mecerreyes, Tailor-made polymer electrolytes based upon ionic liquids and their application in all-plastic electrochromic devices, *Electrochemistry Communications* 8 (2006) 482.
- [10] P. Wang, S.M. Zakeeruddin, J.-E. Moser, M. Grätzel, A new ionic liquid electrolyte enhances the conversion efficiency of dye-sensitized solar cells, *The Journal of Physical Chemistry B* 107 (2003) 13280.
- [11] D.-W. Seo, S. Sarker, N.C.D. Nath, S.-W. Choi, A.J.S. Ahammad, J.-J. Lee, W.-G. Kim, Synthesis of a novel imidazolium-based electrolytes and application for dye-sensitized solar cells, *Electrochimica Acta* 55 (2010) 1483.
- [12] M. Berginc, U. Opara Krašovec, M. Jankovec, M. Topič, The effect of temperature on the performance of dye-sensitized solar cells based on a propyl-methylimidazolium iodide electrolyte, *Solar Energy Materials and Solar Cells* 91 (2007) 821.
- [13] A. Ejigu, K.R.J. Lovelock, P. Licence, D.A. Walsh, Iodide/triiodide electrochemistry in ionic liquids: Effect of viscosity on mass transport, voltammetry and scanning electrochemical microscopy, *Electrochimica Acta* 56 (2011) 10313.
- [14] S. Keskin, D. Kayrak-Talay, U. Akman, Ö. Hortaçsu, A review of ionic liquids towards supercritical fluid applications, *The Journal of Supercritical Fluids* 43 (2007) 150.
- [15] T. Mizumo, E. Marwanta, N. Matsumi, H. Ohno, Allylimidazolium halides as novel room temperature ionic liquids, *Chemistry Letters* 33 (2004) 1360.
- [16] D. Zhao, Z. Fei, W. Ang, P.J. Dyson, Sulfonium-based ionic liquids incorporating the allyl functionality, *International Journal of Molecular Sciences* 8 (2007) 304.
- [17] Z. Fei, D. Kuang, D. Zhao, C. Klein, W.H. Ang, S.M. Zakeeruddin, M. Grätzel, P.J. Dyson, A supercooled imidazolium iodide ionic liquid as a low-viscosity electrolyte for dye-sensitized solar cells, *Inorganic Chemistry* 45 (2006) 10407.
- [18] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, Dissolution of cellulose with ionic liquids, *Journal of the American Chemical Society* 124 (2002) 4974.
- [19] H. Xie, T. Shi, Liquefaction of wood (*Metasequoia glyptostroboides*) in allyl alkyl imidazolium ionic liquids, *Wood Science and Technology* 44 (2010) 119.
- [20] Y. Fukaya, A. Sugimoto, H. Ohno, Superior solubility of polysaccharides in low viscosity, polar, and halogen-free 1,3-dialkylimidazolium formates, *Biomacromolecules* 7 (2006) 3295.
- [21] H.-L. Hsu, W.-T. Hsu, J. Leu, Effects of environmentally benign solvents in the agarose gel electrolytes on dye-sensitized solar cells, *Electrochimica Acta* 56 (2011) 5904.
- [22] I. Soroko, Y. Bhole, A.G. Livingston, Environmentally friendly route for the preparation of solvent resistant polyimide nanofiltration membranes, *Green Chemistry* 13 (2011) 162.
- [23] V.V. Nambodiri, R.S. Varma, Solvent-free sonochemical preparation of ionic liquids, *Organic Letters* 4 (2002) 3161.
- [24] S. Ito, T.N. Murakami, P. Comte, P. Liska, C. Grätzel, M.K. Nazeeruddin, M. Grätzel, Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%, *Thin Solid Films* 516 (2008) 4613.

- [25] T. Singh, T.J. Trivedi, A. Kumar, Dissolution, regeneration and ion-gel formation of agarose in room-temperature ionic liquids, *Green Chemistry* 12 (2010) 1029.
- [26] J.M. Guenet, C. Rochas, Agarose sols and gels revisited, *Macromolecular Symposia* 242 (2006) 65.
- [27] A.W. Baker, A.T. Shulgin, Intramolecular Hydrogen Bonds to  $\pi$ -Electrons and Other Weakly Basic Groups, *Journal of the American Chemical Society* 80 (1958) 5358.
- [28] N. Fatin-Rouge, A. Milon, J. Buffle, R.R. Goulet, A. Tessier, Diffusion and partitioning of solutes in agarose hydrogels: The relative influence of electrostatic and specific interactions, *The Journal of Physical Chemistry B* 107 (2003) 12126.
- [29] H.W. Han, W. Liu, J. Zhang, X.Z. Zhao, A hybrid poly(ethylene oxide)/poly(vinylidene fluoride)/TiO<sub>2</sub> nanoparticle solid-state redox electrolyte for dye-sensitized nanocrystalline solar cells, *Advanced Functional Materials* 15 (2005) 1940.