Electrospun AZO Electrodes and Solid-Stat Electrolyte for Dye-Sensitized Solar Cell

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Abstract

Dye-sensitized solar cells (DSSCs) play important role to convert lights into electric energy since they are manufactured easily and cheap. However, DSSCs do not fit for long run because of the leakage of liquid electrolytes. This paper reports the manufacturing of DSSCs based on a semi-solid electrolyte. The electrolyte and the working electrode were synthesized by electrospinning method. The solid-state electrolyte was prepared from the solution of NaI/I_2/HPA that dropped into fibers electrospun from polyvinyl alcohol (PVA) on the counter electrode. The working electrode was prepared and electrospun from the solution of Zinc acetate (ZnAc)/$AlCl_3$/PVA onto the FTO (fluorine-doped tin oxide) glass. The flow rate of solutions for electrospinning process was adjusted 2, 4, 6 µl/min. The morphology of electrode and electrolyte was tested by scanning electron microscopy (SEM). N719 dye was used as sensitizer. The solar cell performance was examined by Keithley 2602A under illumination of 1000 W/m^2. The flow rate of the solution affected the surface quality of the electrolyte and the working electrode. The best performance of the DSSC was obtained at the flow rate of solution at 2 µl/min both for electrolyte and for electrode. The open circuit voltage (V_{oc}) and the short circuit current density (J_{sc}) of the DSSC were 260.15 mV and 0.596 mA/cm^2, respectively. The efficiency and the fill factor of the DSSC were 0.056% and 36.1%, respectively. No leakage was observed during the testing process of the DSSC and it gave a new challenge for further improvement of the DSSCs.

Keywords: Electrospun, Dye-sensitized solar cell, Solid-state electrolyte, Aluminium-doped zinc oxide

1. Introduction

Dye-sensitized solar cell (DSSC) is a photo-electro-chemical device converting photon energy into electric energy. DSSC is an innovative device since it is cheap and easily manufactured. It consists of electrodes, semiconductors, dyes, and electrolytes. The electrolyte functions as a medium for redox reactions supplying electrons to the dyes. DSSC electrolytes generally used are derived from I_2. However, I_2 electrolyte with a volatile nature [1] does not fit for long run of DSSC because of the leakage. Moreover, DSSC with liquid electrolyte is also less stable. This has encouraged the researchers to conduct advanced study on the development of solid-state electrolyte corresponding to DSSC.

In the solid-state, the performance of DSSC can be affected by many factors, such as ionic conductivity, electron recombination, polymer crystallinity, and surface morphology of solid-state electrolytes. The current density of DSSC has also been strongly influenced by the interface contact between the electrolyte and the semiconductor [2] [3] [4]. All parameters affect the ease and distress of electrons moving. A rougher surface of solid electrolyte has better contact with the rough surface of semiconductor. Surface roughness of the solid electrolyte can be influenced by the ionic concentration of the prepared solution [5] and the concentration of HPA (hetero-poly-acid) [3]. Unfortunately, adjusting the composition of the two materials above is of course very difficult to obtain the controlled-size of surface roughness, which in turn led to uncertainty in the contact between the semiconductor and solid electrolyte.

In addition, developing semiconductors and solid electrolytes into fibers is an interesting issue since the raw materials for both can be dissolved in some polymers. Polymers having conductive properties can be made into fibers by using the electrospinning

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machine. Therefore, the surface roughness of both semiconductors and solid electrolytes can be controlled. The semiconductor used in this study is zinc oxide (ZnO) doped by aluminum (Al). To best of our knowledge, the electrical conductivity of aluminum-doped zinc oxide (AZO) is essentially increased due to the contribution from Al^{3+} ions on substitutional sites of Zn^{2+} ions and Al interstitial atoms as well as from oxygen vacancies and Zn interstitial atoms [6]. Moreover, ZnO has a higher electron mobility compared to TiO_2 [7]. Therefore, in this paper, we report the electrospun aluminum-doped zinc oxide (AZO) electrodes and solid-state electrolyte for DSSC.

2. Materials and Methods

2.1. *Preparation and characterization of semiconductor*

The **PVA solution** for semiconductor was first prepared by dissolving polyvinyl alcohol (PVA, Merck, MW 70000 g/mole) into pure water (1:10 w/w), stirred at 70 °C for 2 hours, and cooled at room temperature for 24 hours. The **ZnAc solution** was prepared from zinc acetate (ZnAc, Merck) dissolved in pure water (1:4 w/w) stirred at 70 °C for 2 hours, and then cooled at room temperature for 24 hours. Synthesizing AZO was done by using $AlCl_3$. The weight ratio of $AlCl_3$ introduced into the ZnAc solution was 4%.

Both PVA and ZnAc solution were then mixed at a mass ratio of 5:1. The gel solution was the coated onto fluorine-doped tin oxide (FTO) glass (Pilkington, TC-15, R = 30 $\Omega.cm^{-2}$) by electrospinning method. The ZnAc/$AlCl_3$/PVA solution at three flow rates of 2, 4, and 6 µl/min were electrospun to produce green fibers. They were subsequently hot-pressed at 130 °C with pressure of 30 kg/cm^2 for 10 min. The substrates were then sintered at a temperature of 550 °C for 4 hours to produce AZO semiconductor coated onto FTO glass.

2.2. *Preparation of solid-state electrolyte*

The solid-state electrolyte was fabricated into two main steps. The green fibers of PVA polymer was firstly electrospun onto counter electrode substrate. The electrolyte solution was then dropped into the green fibers of PVA polymer.

Firstly, poly-vinyl alcohol (PVA, MW 75000, Merck, Germany) was dissolved in the distilled water with a concentration of 1:10 (w/w) under continues stirring and heating at 60–70 °C for 8 hours to make a homogenous solution. The solution was then cooled and kept closed for 24 hours to remove the voids. Synthesizing the solid-state fibers was performed by introducing the PVA solution of 1 mL in the syringe pump of electrospinning machine. The solution at three different flow rates of 2, 4, and 6 µL/min were electrospun onto counter electrode substrate.

To fabricate the solid-state electrolyte, the solution mixed from 3.3 g NaI (99.95%, Merck), 523.9 mg I_2 (Merck), 5.5 mg HPA (Merck), and 30 mL acetonitrile (AN, Merck) was dropped on the green-fibers and dried in atmospheric air.

2.3. *Characterization of materials and DSSC*

Before assembled for DSSC, the crystallinity of semiconductor was examined by X-ray diffraction (XRD). The surface morphology of semiconductor and electrolyte was tested by scanning electron microscopy (SEM).

Furthermore, the AZO semiconductor was immersed in dye N719 for 20 min. The light absorbance for AZO and AZO immersed in dye was examined by ultraviolet-visible (UV-Vis) spectrophotometry. The solid-state electrolyte and the AZO semiconductor were then assembled become DSSC with the order of the flow rate of electrolyte-semiconductor as following: 2-2, 2-4, 2-6; 4-2, 4-4, 4-6; and 6-2, 6-4, 6-6). All cells above were illuminated in Keithley 2602A under irradiation of 1000 W/m^2 by Xenon lamp to examine their performance.

3. Results and Discussion

3.1. *Characterization of semiconductor and solid-state electrolyte*

The respective SEM images of semiconductor and electrolyte are shown in Figure 1 and Figure 4. The AZO was arranged such as grains on the surface of FTO substrate. The increase of flow rate led to reduce the fibers density on FTO. The broken fiber of AZO can be seen more and more on a large flow rate. The broken fibers were caused by hot-pressed employed to increase the adhesion between semiconductor and FTO. In the other hand, many empty areas are also appeared on the surface of FTO substrate. Furthermore, the adhesion of semiconductor fibers and FTO is difficult by using hot-pressed [8]. The fiber diameter of AZO semiconductor was ranging from 45 nm to 393 nm as shown in Figure 1. The thickness of the AZO semiconductor was about 994 nm at a flow rate of 2 µL/min.

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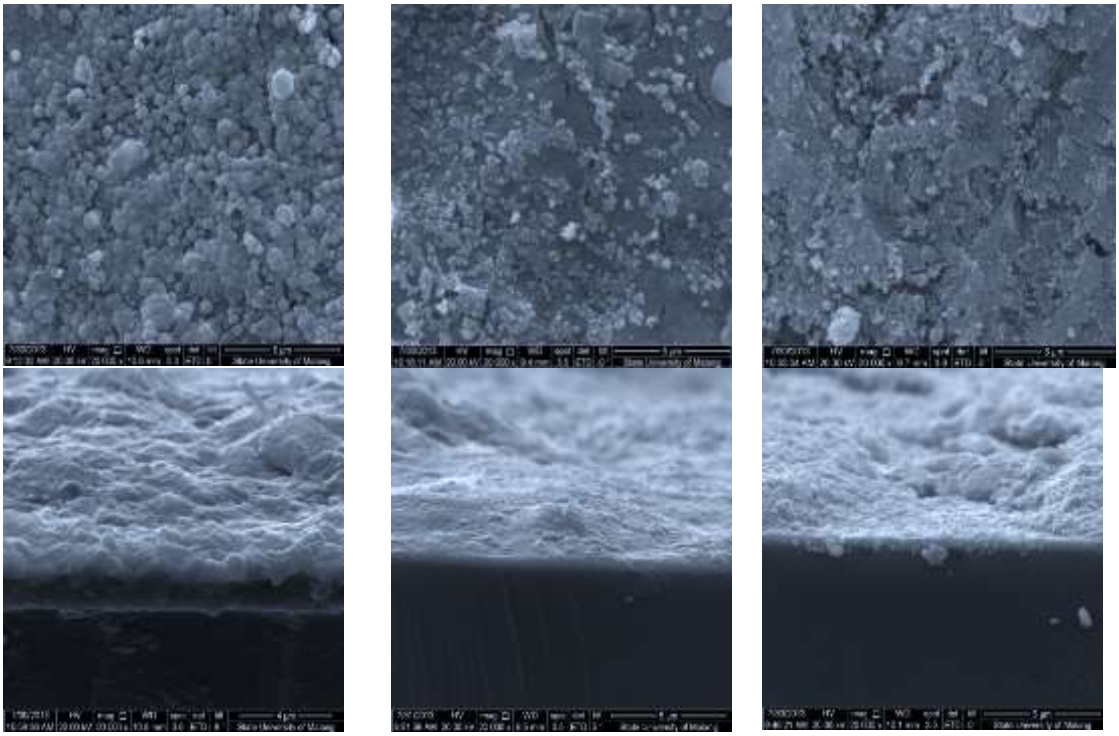
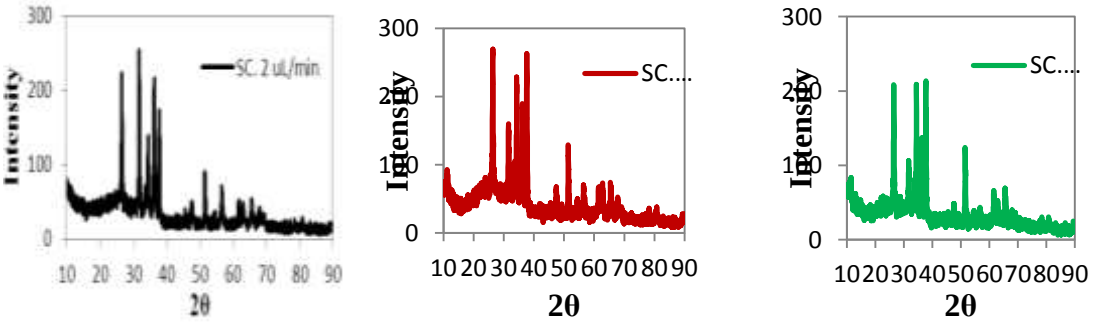


a) 2 µL/min b) 4 µL/min c) 6 µL/min

Figure 1. SEM images of semiconductor

The XRD patterns of semiconductor shown in Figure 2 reveal that the fibers of AZO semiconductor are very thin except for flow rate of 2 µL/min. The XRD pattern showed a combining pattern between AZO and SnO_2. The crystallinity of semiconductor with flow rate of 2, 4, and 6 µL/min was 82.69%, 80.72%, and 76.61%, respectively. Meanwhile, the crystal diameter of semiconductor synthesized at a flow rate of 2, 4, and 6 µL/min was 52.4 nm, 30.1 nm, and 32.1 nm, respectively.



a) 2 µL/min b) 4 µL/min c) 6 µL/min

Figure 2. XRD pattern of semiconductor

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The degree of crystallinity and diameter of crystal has big influence on the transmittance and absorbance of light. Immersing the AZO semiconductor into N719 dye slightly increased the light absorbance as shown in Figure 3. AZO synthesized at a flow rate of 6 µL/min has the highest light absorbance showing the bigger potential to enhance the performance of DSSC.

In addition, Figure 4 shows the SEM images of solid-state electrolyte for various flow rates. SEM images show that the electrolyte samples were not in grains form. The form of electrolyte samples was nano fibers and the fibers mat was capable to adsorb redox couple of I^-/I^{-3}.

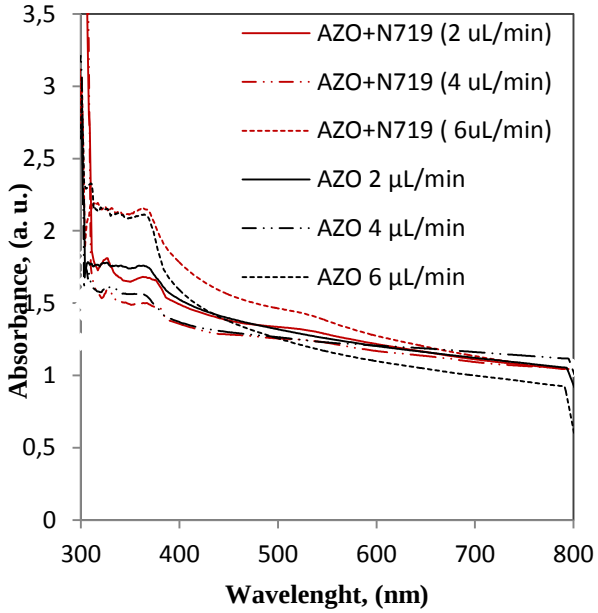
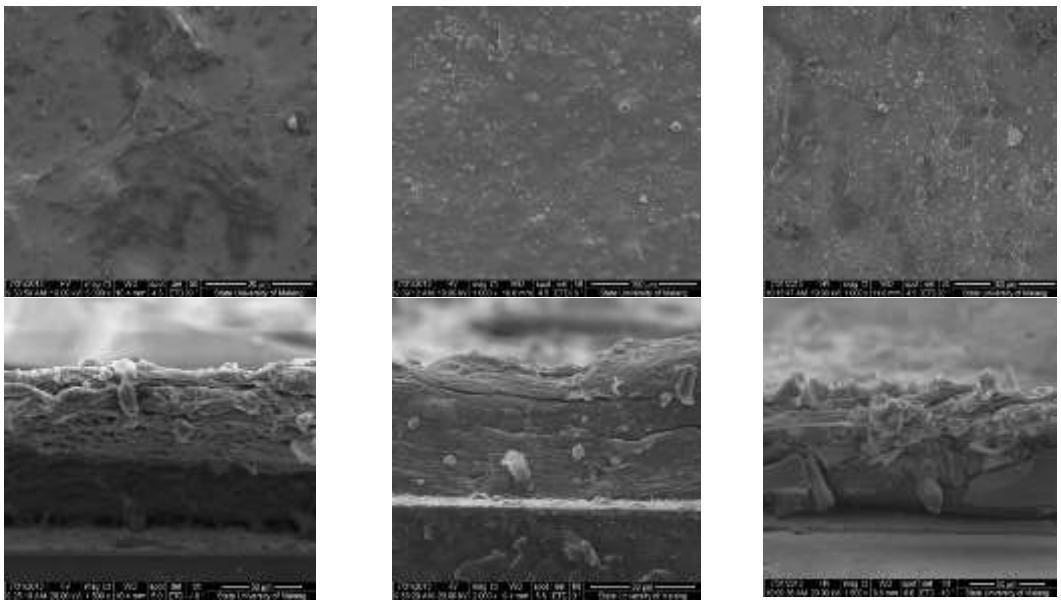


Figure 3. UV-Vis Absorbance curve of semiconductor and semiconductor+N719



a) 2 µL/min b) 4 µL/min c) 6 µL/min

Figure 4. SEM images of solid-state electrolyte

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3.1. *Characterization of DSSC based on solid-state electrolyte*

Table 1 and Figure 5 show that the short-circuit current density (J_{sc}) in cell 2-2 was higher than that in cell 2-4 and cell 2-6. The lower the flow rate for synthesizing the electrolyte, the higher the J_{sc} and efficiency of DSSC was achieved. As shown in Figure 4, the poor porosity and surface morphology were detected with increasing flow rate of solution to synthesize the electrolyte leading to reducing the electrolyte absorbed in the electrolyte. Table 1 and Figure 5 feature also the effect of the flow rate of solution to synthesize the semiconductor on the performance of DSSCs. Bigger flow rate led to reduce the efficiency of solar cells because the breaking of fibers resulted with high flow rate was more pronounced when applied hot-pressed. The breaking fibers led to reduce the contact quality between semiconductor and solid-state electrolyte and therefore increase the total resistance in the DSSC as shown in Table 1.

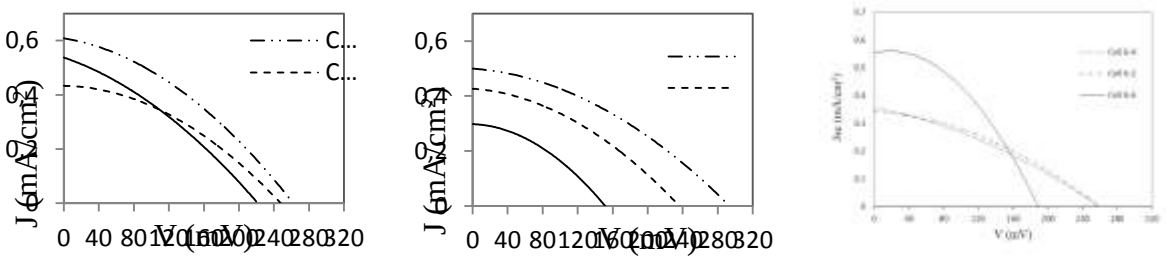

Figure 5. I-V curve of DSSCs

Table 1. Characteristic of DSSC

No.	**Flow rate** (µL/min)		R_{total} (kΩ)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	η (%)
	Electrolyte	Semiconductor					
1	2	2	6.88	0.610	260	35.30	0.056
2		4	8.36	0.433	250	37.30	0.040
3		6	8.60	0.544	220	31.30	0.037
4	4	2	8.65	0.508	290	35.50	0.052
5		4	8.90	0.427	240	35.40	0.036
6		6	10.01	0.300	153	36.00	0.016
7	6	2	8.22	0.357	260	32.23	0.030
8		4	7.70	0.350	260	34.85	0.032
9		6	7.20	0.544	190	38.14	0.013

Generally, the entire DSSCs generated a low open circuit voltage (max 300 mV) and low short circuit current. In addition, the DSSC with semiconductor and electrolyte with flow rate of electrospinning 2 µL/min has better performance than that of other DSSCs. There are many factors influencing to the performance of DSSC such as types of dyes, functional groups of dyes, types of semiconductors, form of semiconductors, transport of electrons from electrolytes to dyes, ionic conductivity of electrolyte, etc. For semi-solid DSSC, beside many factors above, the surface contact between the electrolyte and the semiconductor [1] and the surface morphology of the semiconductor and the electrolyte [3] may have significant influence to the performance of DSSC. However, the results of SEM images in Figure 1 and the performance of DSSC (Table 1) show that Jsc was strongly affected by the quality of surface contact between the electrolyte and the semiconductor. SEM images show that the semiconductor surface discharged at 2 µL/min was denser, more compact, and with larger particles size. In the other hand, the electrolyte surface discharged at 2 µL /min was more rugged as shown in Figure 4.

Because the contact between the two surfaces of semiconductor and electrolyte was better, then the transport of electrons from the electrolyte to the semiconductor was smoother. In addition, another factor that might affect to the Jsc was absorbance. However, effect of absorbance of the performance of the DSSC is less pronounced than that of the quality of surface contact between semiconductor and electrolyte.

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4. Conclusion

Electrospun AZO electrodes and solid-state electrolyte has been synthesized and used for DSSC. The flow rate of solution has strong effect on the quality of both semiconductor and electrolyte. The semiconductor surface discharged at 2 μL/min was denser, more compact, and with larger particles size. Meanwhile, the electrolyte surface discharged at 2 μL /min was more rugged. Both conditions result in a better quality of surface contact between semiconductor and electrolyte and therefore produce the highest performance of the DSSC. The best performance of the DSSC was obtained at the flow rate of solution at 2 μl/min both for electrolyte and for electrode. The open circuit voltage (V_{oc}) and the short circuit current density (J_{sc}) of the DSSC were 260.15 mV and 0.596 mA/cm^2, respectively. The efficiency and the fill factor of the DSSC were 0.056% and 36.1%, respectively. No leakage was observed during the testing process of the DSSC and it gave a new challenge for further improvement of the DSSCs. Further study to improve the quality of the surface contact between electrolyte and semiconductor and between FTI and semiconductor is needed to further improve the performance of solid-state DSSC.

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