エネルギー変換を経て水素ガスの作成に
なる研究を表記

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Abstract

Series circuit of six organic thin-film solar cells (OSCs) consisting of poly(3-hexylthiophene) and PCBM has been fabricated in order to electrolyze water into hydrogen and oxygen gases. The open circuit voltage increases linearly with the number of unit cells and becomes 2.9 V at the six unit cells. On the other hand, the short circuit current, the fill factor and the energy conversion efficiency are almost constant, independent of the number of unit cells. The series circuit of six OSCs was combined with the water electrolysis cell with two platinum electrodes. Hydrogen and oxygen gases were generated at each platinum electrodes of the electrolysis cell under illumination. The operating current and voltage was determined to be 1.3 mA/cm² and 2.6 V, respectively.
Introduction

Solar energy utilization is important issue for sustainable energy sources. However, drawback of the sunlight is various fluctuations, such as daytime, weather and season fluctuations. So, to use the solar energy stably at anytime, it is necessary to storage to rechargeable batteries or to convert into high energy materials like photosynthesis. Therefore, we try to convert water into hydrogen and oxygen gases as high energy materials using electric power produced by solar cell. Recently, bulk heterojunction (BHJ) organic thin-film solar cells (OSC) composed of poly(3-hexylthiophene) (P3HT) as a donor and [6,6]-phenyl C61 butyric acid methyl ester (PCBM) as an acceptor have been greatly investigated because of flexibility, low cost and good processability. [1] However, the open circuit voltage (Voc) has been reported to be less than 0.6 V, which is too low to operate electrolysis of water to hydrogen and oxygen gases. There are several approaches to make Voc higher, such as synthesis of new low band gap polymers [2,3] and construction of hierarchical film structures of OSCs. [4,5] However, it is difficult for the unit cell of the advanced OSCs to electrolyze water so far. Therefore, we think out that the series circuit of several OSCs on one chip can produce enough voltage to converts water into hydrogen and oxygen gases. We design the series circuit consisting of six unit cells of OSC.

Experiments

The series circuit of six OSCs was designed on 2.5 × 2.5 cm$^2$ ITO glass as shown in Fig. 1. The construction of the OSC was almost the same as literatures. [1]

Briefly, the monochlorobenzene solution of P3HT and PCBM (1:1 w/w, 20 mg/mL) was spincoated onto the patterned ITO surface. The P3HT/PCBM film was annealed at 120 °C for 2 min to make bicontinuous morphology. And then LiF as a hole blocking layer and Al as a cathode onto the annealed P3HT/PCBM films were vacuum-deposited through the shadow mask for restricting the active area of 0.4 cm$^2$, successively. The film thickness of LiF and Al is 0.5 and 100 nm, respectively. The solar cells were evaluated at room temperature in an air condition. Current (I) – voltage (V) measurements of the series circuit of OSCs and the combination of the water electrolysis and the series circuit of OSCs were performed using a Keithly 2400 SourceMeter and 100 mW/cm$^2$ xenon lamp with AM 1.5G solar filter. The water electrolysis cell consisted of an H-shape glass cell in
0.1 M H$_2$SO$_4$ solution with two platinum wire electrodes (0.8 mm$\phi \times 2.0$ cm) to measure generated gas volume. I-V measurement of the water electrolysis was carried out using potentiostat (VersaSTAT3, Princeton Applied Research).

**Results and Discussion**

To clarify the voltage for water electrolysis, we measured current-voltage curve at electrolysis cell with two Pt electrodes in 0.1 M H$_2$SO$_4$ solution as shown in Fig. 2(A).

Pt was selected because of lower overpotential for water electrolysis than the other electrode materials. Although the theoretical voltage for water electrolysis is thermodynamically 1.24 V [6], the current does not flow practically at the voltage. The onset voltage where the current begins to flow is around 1.6 V because of need of the overpotential to electrolyze water kinetically. Moreover, to get current value of 1.0 mA/cm$^2$, the voltage of 1.8 V is needed according to Butler-Volmer equation [6] and the existence of solution resistance. Therefore, it is necessary for OSC to electrolyze water at the operating voltage of more than 1.8V. The unit cell of OSC was characterized at first to decide the number of the unit cells for the series circuit of OSCs to electrolyze water (Fig. 3). The dark current shows the typical p-n junction diode’s characteristics (Fig. 3b). The performance of the unit cell of OSC under the simulated sun light (Fig. 3a) was Voc of 0.46 V, short circuit current (Jsc) of 5.2 mA/cm$^2$, fill factor (FF) of 0.39 and energy conversion efficiency ($\eta$) of 0.93 %. The values of Jsc, Voc were similar to the reported ones but those of FF and $\eta$ were lower [1] because it might be slightly different fabrication conditions. Since this Voc is too low to electrolyze water, we designed and characterized the series circuit of six OSCs. Although the series circuit of four unit cells of OSC is enough to get Voc more than 1.8 V, the number of the unit cells over four should be needed to ensure both of the operating voltage and current for water electrolysis. So, we designed the series circuit of six unit cells of OSC and characterized (Fig. 3c).

Voc of the series circuit of OSCs increased linearly with the number of the unit cells and became 2.9 V at the six unit cells. The dark current obtained at the series circuit of 6 OSCs began to flow at higher bias voltage than that at one unit cell (Fig. 3d). Jsc, FF and $\eta$ are almost constant to be 4.74 mA/cm$^2$, 0.46 and 1.07 %, respectively,
independent of the number of unit cell. The series circuit of 6 OSCs was combined with the water electrolysis cell consisting of two platinum wire electrodes in 0.1 M H$_2$SO$_4$ solution. The water electrolysis did not happen at the lower bias voltage, which was inversed against the voltage generated at the OSC, than around 2.5 V but the inversed water electrolysis reaction took place over 2.5V under the dark condition (Fig. 2B, curve (b)). When the simulated solar light was irradiated at the series circuit of 6 OSCs for 10 min, hydrogen and oxygen gases were generated at each platinum electrodes of the electrolysis cell. The maximum operating current was observed to be 1.3 mA/cm$^2$ at no bias voltage (Fig. 2B, curve (a)). The operating voltage applied at the electrolysis cell was calculated to be 2.6 V from Fig 3c. The electrolyzing current decreased with increasing bias voltage because the voltage applied at the water electrolysis cell was reduced. When the bias voltage of 1.3 V is applied, the current did not flow and the voltage applied at the water electrolysis cell is calculated to be 1.6 V from Voc of 2.9 V. This voltage is identified to that obtained at the water electrolysis using potentiostat from Fig. 2A. Unfortunately, the volume of generated hydrogen and oxygen gases could not be quantitatively measured because of too small active area of the unit cell of the OSC.

**Conclusion**

The series circuit of 6 OSCs was fabricated and the Voc increased six times compared with that of the unit cell without any significant change of other parameters such as Jsc, FF and $\eta$. The combination of water electrolysis cell and the series circuit of 6 OSCs enables us to convert water into hydrogen and oxygen gases. The quantification of hydrogen and oxygen gases using larger active area of the OSCs is under investigation.

**Acknowledgement**

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**References**


Figure captions

**Figure 1.** Schematic representation of the series circuit of 6 OSCs from the top view (a) and the cross-section (b).

**Figure 2.** (A) I-V curve for water electrolysis with two Pt electrodes at scan rate of 50mV/s in 0.1M H$_2$SO$_4$ solution. (B) I-V curves obtained at the water electrolysis connected with the series circuit of 6 OSCs under light (a) and in the dark (b).

**Figure 3.** I-V curves obtained at the unit cell of OSC under light (a) and in the dark (b) and the series circuit of 6 OSCs under light (c) and in the dark (d).
Figure 1 Schematic representation of the series circuit of 6 OSCs from the top view (a) and the cross-section (b).
Figure 2 (A) I-V curve for water electrolysis with two Pt electrodes at scan rate of 50mV/s in 0.1M H$_2$SO$_4$ solution. (B) I-V curves obtained at the water electrolysis connected with the series circuit of 6 OSCs under light (a) and in the dark (b).
Figure 3 I-V curves obtained at the unit OSC under light (a) and in the dark (b) and the series circuit of 6 OSCs under light (c) and in the dark (d).