

Series circuit of organic thin-film solar cells for electrochemical conversion of water into hydrogen

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Solar light is among the most studied sustainable energy sources for energy harvesting. However, the drawbacks of using sunlight are daytime, weather, and seasonal fluctuations. So, to use solar energy stably at any time, it is necessary to store energy in rechargeable batteries or to convert energy into high-energy materials. One possibility to produce high-energy materials by using solar energy is to convert water into hydrogen (so called "solar hydrogen") and oxygen gases. There are mainly two approaches for this kind of conversion, either using electric power produced by solar cells or by directly applying photocatalysis. Conversion through electric power has an advantage, in that voltage can be increased by connecting several cells in series, whereas sunlight is limited to wavelengths shorter than the visible when applied in photocatalysis. Hydrogen is a valuable source for fuel-cell vehicles, co-generation systems producing electric power and hot water with the help of a fuel cell, and as a chemical reagent for hydrogenation or as a reductant instead of oil and natural gas.

Bulk hetero-junction (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 investigated thoroughly owing to their flexibility, low cost, and good processability. The open circuit voltage (V_{oc}) has been reported to be less than 0.6V, which is too low to convert water to hydrogen and oxygen gases by electrolysis. There are several approaches to increase V_{oc} , such as the synthesis of new low-band-gap polymers, the construction of hierarchically structured OSC films, tandem solar cells. However, for a single unit cell of such advanced OSCs it is still difficult to electrolyze water. Therefore, we investigated how the series circuit of several OSCs on one chip can produce enough voltage to convert water into hydrogen and oxygen gases. We found that a series circuit consisting of six OSC unit cells is enough to convert water into hydrogen and oxygen gases at optimum power conversion efficiency.

To clarify the voltage for water electrolysis, we measured cyclic voltammograms with various electrodes such as glassy carbon (GC), Pt, carbon-supported Pt nanoparticle (PtC), and Ni electrodes in 0.1M H_2SO_4 solution. The voltammogram with the GC electrode shows almost no current between 1.5 and 1.8V versus SCE, indicating that neither hydrogen nor oxygen is produced. Meanwhile, the Pt electrode shows a cathodic current around 0.5V and an anodic current around 1.5V versus the SCE, which means that there is an evolution of hydrogen and oxygen. Although the theoretical thermodynamic voltage for water electrolysis is 1.23V, practically no current flows at this voltage when using an electrolysis cell with a Pt anode and a Pt cathode. To receive a current value of 1.0mAcm^{-2} , a voltage of 1.8V is needed according to the Butler-Volmer equation and the existence of a solution resistance. Thus, the OSCs should be able to electrolyze water at an operating voltage higher than 1.8V. We also investigated water electrolysis using

other electrodes, such as PtC electrodes, which have the advantage of needing less expensive Pt. Similar cathodic current flows compared to Pt wire electrodes were measured using PtC electrodes, and hydrogen was generated. In contrast, we used a Ni electrode as anode because of carbon corrosion of PtC.

As OSCs composed of P3HT as donor and PCBM as acceptor are standard and well-known organic solar cells, this kind solar cell was selected as the unit cell for our series circuit. First, the single unit cell was characterized to determine the number of the unit cells needed for an OSC series circuit being capable of electrolyzing water. The performance of such a unit cell under simulated sunlight was $V_{oc}=0.46\text{V}$, the short circuit current (J_{sc}) 5.2mAcm^{-2} , the fill factor (FF) 0.39, and η was 0.93%. Since the measured V_{oc} for one unit cell is too low to electrolyze water, we designed and characterized the series circuit of six OSCs. Although a series circuit of four OSC unit cells is enough to achieve a V_{oc} value higher than 1.8V, the use of more than four unit cells ensures the operating voltage and the current needed for water electrolysis. Thus, we designed and characterized a series circuit of six OSC unit cells.

The dependence of the solar cell characteristics on the number of unit cells (n) in the series circuit is investigated. V_{oc} increases linearly with n and reaches 2.9V for $n=6$. J_{sc} , FF, and η are approximately constant with values of 4.74mAcm^{-2} , 0.46, and 1.07%, respectively, thus, independent of the number of unit cells. The dependence of the electric power on voltage shows a triangular shape, which means that the electric power is zero under short circuit and open circuit conditions, and the maximum value is found between these two boundaries. The maximum electric power increases with the number of unit cells similar to V_{oc} . A maximum electric power of 8.86mWcm^{-2} was obtained at 2.35V. Thus, the voltage should be employed when electrolyzing water with a series circuit of six OSC unit cells.

The series circuit of six OSCs was combined with a water electrolysis cell consisting of two Pt wire electrodes in a 1.0M H_2SO_4 solution. The I-V performances without the electrolysis cell were characterized as irradiated. The obtained values for J_{sc} , V_{oc} , FF, and η prior to irradiation were 4.94mAcm^{-2} , 3.4V, 0.53, and 1.47%, respectively. I-V performances for the series circuit of six OSCs with the electrolysis cell were also characterized. The voltage indicates an inverse bias voltage against the electrolyzing voltage. The observed electrolyzing current is 3.7mAcm^{-2} at no inverse bias voltage. The applied electrolyzing voltage to the electrolysis cell was 2.3V and stayed constant during light irradiation. Thus, the series circuit of six OSCs was operating at the maximum electric power mentioned above. When the simulated solar light irradiated the series circuit of six OSCs for 60min, hydrogen and oxygen gases were produced at the Pt electrodes of the electrolysis cell. The volume of generated hydrogen and oxygen gases increased linearly with irradiation time and reached 0.65 and 0.25mL for 60min irradiation.

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