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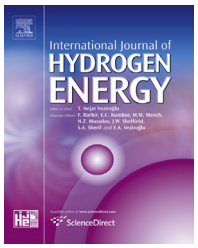

Characteristics of hydrogen generation from water splitting by polymer electrolyte electrochemical cell directly connected with concentrated photovoltaic cell

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ABSTRACT

Energy storage is a key technology for establishing a stand-alone renewable energy system. Current energy-storage technologies are, however, not suitable for such an energy system because the technologies are cost ineffective and achieve low energy-conversion efficiency. The most realistic and expected technology is hydrogen generation from water splitting by an electrochemical cell directly connected with photovoltaic cell. In this study, a simple concept is proposed for generating hydrogen from water splitting by using a direct-electrically-connected polymer electrolyte electrochemical cell and a separately-located concentrated photovoltaic cell, named a "concentrated photovoltaic electrochemical cell (CPEC)". The CPEC operates stably and achieves relatively high-energy conversion efficiency from light to hydrogen of over 12%. The conditions are comparison with those of the electrochemical cell connected with a polycrystalline Si solar cell.

1. Introduction

In preparation for the exhaustion of fossil fuels, energy storage of renewable energy needs to complement its capricious nature. Compared with technologies for power generation using solar cells, conventional energy-storage techniques have been underdeveloped. Rechargeable batteries, like lithium-ion batteries, are too expensive to be used as storage devices for renewable-energy systems. "Concentrated solar power" (CSP) is a relatively recently established technology for

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storing sunlight as thermal energy. The storing temperature by CSP is relatively high at around 500 °C (67 meV), but it has energy loss larger than the maximum energy of sunlight energy, which is a few electron-volts. On the other hand, sugar production by using algae or plants is another option, but the energy-conversion efficiency of photosynthesis is said to be less than 1%. Therefore, hydrogen generation using water splitting by sunlight energy is expected to be an alternative energy-storage method.

Photoelectrochemical water splitting using semiconductor particles or electrodes is attracting much attention as a hydrogen production technique by water splitting. It is expected to use sunlight energy of over 50% to generate hydrogen. In energy conversion from sunlight to hydrogen, however, the photoelectrochemical water splitting is currently inferior to the electrochemical water splitting by using electricity generated by solar cell. The cells are usually single, polycrystalline, or amorphous Si solar cells. Since the open-circuit voltage (V_{oc}) of a Si solar cell is around 0.6–0.7 V, the voltage is insufficient to split water (1.23 V). Thus, the water splitting system has to be the series connection number of solar cells and electrochemical cells [1,2]. In addition, the energy conversion efficiency of the cells from sunlight to electricity is usually 10–20% (maximum record is 25.0%). This is the upper limit of the energy conversion efficiency from sunlight to hydrogen. Even with these difficulties, the current conversion efficiency from sunlight to hydrogen is over 12% under stable operation [1].

To overcome the difficulties, the usage of a photovoltaic cell with multiple junctions has been proposed. It is not clear when the idea was first published, but the concept was clearly proposed in 1998 by Khaselev and Turner [3]. They used the multiple junction photovoltaic cell as a photocathodic electrode. Soon after the report, the idea of the separation of photovoltaic cell and electrochemical electrode was proposed in 2000 by Licht et al. [4]. They indicated that the possible conversion efficiency from sunlight to hydrogen was up to 30% by using $Ga_xIn_{1-x}P/GaAs$ double-junction solar cell system with/without light concentration. Their experimental photohydrolysis system was an $Al_xGa_{1-x}As/Si$ double-junction solar cell directly attached to Pt black and RuO_2 electrodes dipped into 1.0 mo/L $HClO_4$ aqueous solution. The energy conversion efficiency from sunlight to hydrogen was 18.3% under AM0 (130 mW/cm^2).

The next important step was demonstrated by the Fraunhofer Institute group [5,6]. The hydrogen generation was performed by a $Ga_xIn_{1-x}P/Ga_yIn_{1-y}As$ double-junction solar cell system and a polymer electrolyte electrochemical cell (PEEC) using Pt-cathode and Ir-anode under 500-times solar light concentration. The unique characteristics are the electrochemical cell directly attached under the double junction solar cell and the usage of PEEC. The electrolyte for PEEC is proton exchanging polymer membrane, thus the system does not require conductive aqueous electrolytes and pure water is used as the source of hydrogen. The energy conversion efficiency from real sunlight to hydrogen was 15.1% from the recalculation with hydrogen energy of 1.23 V. The efficiency was reported to be 18.1% with hydrogen energy of 1.48 V.

Both of these typical systems using electrochemical electrode are specifically designed for water splitting by solar energy. The systems require unique electrochemical and solar cells. In addition, the optimized operating conditions for high conversion efficiency are obscured due to the complicated system design. To establish a "stand-alone total natural energy" system for not only energy generation but also energy usage, a high-efficiency and simple device is suitable for converting sunlight into storage energy [7]. In addition, the separation of electricity and hydrogen generation is indispensable because the energy storage device must be used in conjunction with other energy sources like water and/or wind power generation. Therefore, this paper proposed a much simpler water-splitting hydrogen generation system, which is a combination of a PEEC and a concentrated photovoltaic cell (CPV). Since the PEEC and CPV can be set separately, the system establishes much more flexibility from the design point of view. Moreover, the operating conditions can be measured easily. Thus, the suitable operating conditions, especially for the origin of the energy loss for the water splitting hydrogen generation are also discussed.

2. Experimental procedure

The proposed "concentrated photovoltaic electrochemical cell" (CPEC) system consists of a PEEC and a CPV. The PEEC and CPV are separately set and directly connected electrically without any intermediate conversions. The CPV used was a GaInP/InGaAs/Ge 3-tundem cell with a surface area of 1.0 × 1.0 cm^2 square (Spectrolab Inc., C3MJ5 PP-06491-CCC "CDO-100"; Typical cell efficiency of 39.2%) [8–10]. The PEEC was a platinum-loaded carbon paper electrode with a proton exchange polymer membrane as an electrolyte with 4.0-cm^2 electrode area (H-TEC EDUCATIONS GmbH, Electrolyser 5-E101). Pure water was used as a splitting source. The schematic system design of CPEC is shown in Fig. 1. The CPV was illuminated by concentrated light of AM1.5G solar simulators instead of the concentrated sunlight (Ushio Corp., SX-UID502XQ). No cooling equipment was used for the CPV, so the cell temperature rose with increasing light intensity and operation time. The CPEC system was compared with a combination of PEEC and conventional polycrystalline Si (c-Si) solar cell instead of CPV. The multiple-series electrical junction of PEEC and CPV was also used.

3. Results and discussion

3.1. *Properties of polymer electrolyte electrochemical cell (PEEC)*

The sunlight to hydrogen energy conversion efficiency (η_{StH}) for the combination system of electrochemical and solar cell is described; $\eta_{StH} = \eta_{StE} \times \eta_{EtH}$, where η_{StE} is the efficiencies of sunlight to electricity by solar cell and η_{EtH} is the efficiency of electricity to hydrogen by electrochemical cell. In this study, the light source is not real sunlight but a solar simulator, thus the efficiency used is not η_{StH} but that of light to hydrogen energy (η_{LtH}). The definition of η_{LtH} is similar to that of η_{StH}; $\eta_{LtH} = \eta_{LtE} \times \eta_{EtH}$, where η_{LtE} is the efficiencies of illuminated