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From solar photocatalysis to fuel-cell: A hydrogen supply chain

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ABSTRACT

Solar hydrogen production coupled with a fuel cell stack would appear to be an alternative method to produce environmentally friendly energy and could overcome the intermittent nature of the power sources. In particular, production of hydrogen in a solar photocatalytic reactor using wastewater offers a promising way forward. A system combining photoreactors for hydrogen production by photocatalytic methanol dehydrogenation and a proton exchange membrane fuel cell (PEMFC) was used to directly convert solar irradiance into electricity. The photoreactor system of about 364 cm^2 contains 1.2 L of pure methanol and a TiO_2 slurry of 1 g/L. The fuel cell presents a 25 cm^2 active area filled at the anode by photocatalytic hydrogen and at the cathode by oxygen from the air in a self-breathing mode. Fuel cell performances have been followed at constant voltage. Without any purification of hydrogen and without any optimization of the design, the system successfully provides an electric power density of 1 mW cm^{-2} of photoreactor optical surface area exposed to the sunlight.

1. Introduction

Hydrogen and its potential use in a fuel cell could be an efficient and a clean energy carrier.

Among the different fuel cells, the Proton Exchange Membrane Fuel Cell (PEMFC) would appear to be a promising energy converter for various power applications from small mobile applications (3–5 W) to transport application (80 kW). Coupling the hydrogen oxidation reaction (HOR) at the anode and oxygen reduction reaction (ORR), the PEMFC produces electricity, heat and water as by-products.

However, current hydrogen production methods are mainly related to fossil fuels. As an example, steam methane reforming (SMR) is one of the most developed ($\approx$ 49%) and low-cost methods for producing hydrogen [1]. To limit fossil fuel use, renewable resources are being extensively investigated. Solar energy is a renewable and abundant resource that could be used in many ways to produce hydrogen through electrolysis, thermolysis, thermochemical cycles, photoelectrolysis and biophotolysis [2].

Photovoltaic cells coupled with water electrolysis are one of the most developed methods to convert solar energy into electricity. The efficiency of current photovoltaic cells to convert solar irradiance into electricity is about 10–20% [3]. Water electrolysis demonstrates a really efficient way to convert electricity into hydrogen (50–80%). The best efficiency for this method of directly converting solar energy into hydrogen is 16% [4,5]. Considering that current proton exchange membrane fuel cells (PEMFC) have a yield of 47 % on the conversion of hydrogen into electricity, the global yield of this system to convert solar energy into electricity is about 8%.

Alternative methods, to produce hydrogen, such as photobiological process which uses the photosynthesis of micro-organisms [2,6,7] or photocatalysis [8–12] are carried out mainly at laboratory-scale or pilot-scale. The possibility of producing hydrogen from organic wastewater by photocatalysis, as for other methods [13], with solar energy is a very attractive way. Presently, alcohol is often used as model feedstock with or without water to produce hydrogen via a reforming reaction [9,10] or dehydrogenation reaction [9,11,12]. Methanol is often found to be the best reactant for producing hydrogen via photocatalysis [12,14]. A bifunctionnal reaction mechanism for photocatalytic alcohol dehydrogenation was proposed [12,15]. This mechanism combines a photocatalyst (TiO_2), which absorbs photons with energy higher than its band gap and absorbs alcohols at its surface, and a metallic cocatalyst (platinum as example), deposited onto the surface of the catalyst. This improves the electron/hole pair separation and is able to reduce protons into hydrogen. The P25 from Evonik is known to be one of the most efficient TiO_2 for most photocatalytic reactions, while platinum remains the best cocatalyst with a minimal loading for hydrogen production [9,16,17]. The alternative

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Nomenclature

PEMFC	Proton exchange membrane fuel cell
DMFC	Direct methanol fuel cell
OCV	Open circuit voltage
I	Current (A)
U	Voltage (V)

of directly feeding a PEMFC with hydrogen produced in a new experimental method was performed for photobiological synthesis [18] and for photocatalysis [19,20].

Furthermore Direct Methanol Fuel Cells (DMFC) can utilize methanol and directly produce electricity but they suffer because of methanol crossover toward the cathode which drastically reduces their efficiency to about 20% [21].

The aim of this work is to demonstrate a hydrogen supply chain which includes hydrogen production (by photocatalysis), hydrogen storage and hydrogen use in a fuel cell. The possibility to directly use solar irradiance to produce electricity with a system combining hydrogen production by photocatalysis (methanol dehydrogenation) and a proton exchange membrane fuel cell would appear to be interesting. Fuel cell performance was followed under different operating conditions by applying a constant voltage.

2. Experiment

Titanium dioxide P25 (Aeroxide, P25) from Evonik was used as the photocatalyst and hexachloroplatinate acid (Sigma-Aldrich, H_2PtCl_6, $6H_2O$) as the platinum salt. Methanol (Fisher Chemical, 99.99%) was used as model feedstock for photocatalytic alcohol dehydrogenation reaction.

The experimental setup for direct solar conversion into electricity, including photoreactors and an air-breathing fuel cell, is shown in Fig. 1.

The photocatalytic system consists of 4 photoreactors and an aluminium reflector. Each photoreactor consists of a 26 cm long Pyrex cylinder with a base diameter of 3.5 cm corresponding to a direct optical area of 91 cm^2 as described above [19]. The aluminium reflector was used to optimize irradiation of the slurry with solar light. The photocatalytic system and more specifically the aluminium reflector was continuously oriented to track and face the sun. Photoreactors were linked in parallel for liquid circulation, with a recirculating pump, and they shared their gas phase. The total methanol volume was 1.2 L. TiO_2 nanoparticles (1.0 g L^{-1} concentration) were maintained in suspension in methanol through liquid circulation. The Pt/TiO_2 catalyst was prepared via direct photo-deposition of hexachloroplatinate acid under solar irradiation during the experiment, with 1.0 wt.% platinum loading. Indeed absorption of photons on TiO_2 generates an electron/hole pair. The hexachloroplatinic ions on the surface of the catalyst (TiO_2) are reduced by the photogenerated electrons and at the same time methanol is oxidized by the photogenerated holes, as:

$$PtCl_6^{2-} + 2CH_3OH = Pt^{\circ} + 2\ CH_2O + 4H^+ + 6Cl^-$$

The pump allowed the stirring and homogenization of the catalyst/reagent mixture by the recirculation circuit. Photoreactors were purged with helium at 20 mL min^{-1} for thirty minutes before each experiment to remove air/O_2 from the photoreactor and the hydrogen stream. The hydrogen produced by photocatalysis is stored in a 200 mL tank. A valve and a manometer are used to limit, if necessary, the pressure of hydrogen to 0.2 bar. This system played the role of a hydrogen storage media. The PEMFC was an air-breathing fuel cell from PaxiTech. The membrane electrode assembly had an active area of 25 cm^2 and contained a 50 μm thick Nafion membrane with a Pt/C catalyst on the cathode side and Pt-Ru/C catalyst on the anode side. Cathode platinum loading was 0.5 mg cm^{-2}. Catalysts loading at the anode compartment were 0.25 mg cm^{-2} platinum with 0.25 mg cm^{-2} ruthenium. The cell worked with air on the cathode side and hydrogen produced on the anode side. After purging the system with helium, the helium flow was stopped. The end valve remained open during the

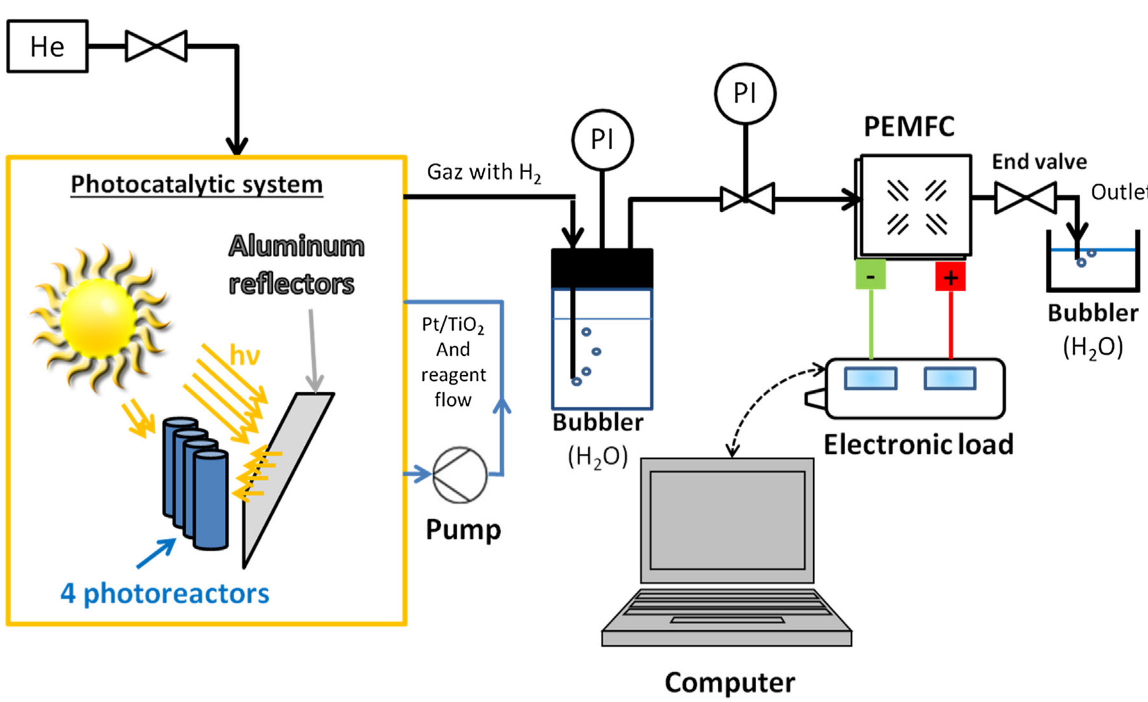

Fig. 1. Experimental setup for solar conversion into electricity using 4 photoreactors and an air-breathing PEM fuel cell.