Electrochimica Acta 182 (2015) 280–288

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Performance characteristics of a membraneless solar responsive photocatalytic fuel cell with an air-breathing cathode under different fuels and electrolytes and air conditions

Lin Li[a,b], Shao Xue[a], Rong Chen[a,b,*], Qiang Liao[a,b], Xun Zhu[a,b], Zhibin Wang[a,b], Xuefeng He[a,b], Hao Feng[a,b], Xiao Cheng[a,b]

[a] Key Laboratory of Low-grade Energy Utilization Technologies and Systems (Chongqing University), Ministry of Education, Chongqing 400030, China
[b] Institute of Engineering Thermophysics, Chongqing University, Chongqing 400030, China

ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form 21 July 2015
Accepted 16 September 2015
Available online 21 September 2015

Keywords:
photocatalytic fuel cell
alkaline electrolyte
alcohol and saccharide
complex wastes
oxygen concentration

ABSTRACT

In this work, a membraneless photocatalytic fuel cell (PFC) with a solar responsive photoanode and an air-breathing cathode was developed to simultaneously degrade the wastewater and generate electricity. The performance characteristics of the developed PFC was examined for the real application purpose. Particular attention was paid to investigate the effect of the fuel and electrolyte types on the cell performance. Experimental results showed that the alkaline electrolyte yielded the maximum power density of 4.1 mW cm^{-2}, which was much better than the neutral electrolyte with the maximum power density of 0.5 mW cm^{-2}. Long-term performance measurements also showed that the cell performance was rather stable under the alkaline electrolyte but dramatically reduced under the neutral electrolyte in the 3-hour constant current density operation. Regarding the fuel types, the PFC exhibited appreciable performance for both alcohols and saccharides. Methanol and glycerol produced the maximum power densities of 4.08 and 2.58 mW cm^{-2}, while D-glucose and D-xylose generated the maximum power densities of 3.92 and 3.67 mW cm^{-2}, respectively. The difference in the cell performance can be attributed to the difference in the molecular structure, i.e., the fuel with a simpler molecular structure and a shorter carbon chain could yield better performance. Besides, the PFCs also showed favorable performances in some complex wastes, such as artificial sewage, Coca Cola and urine. For the air-breathing cathode design, the oxygen concentration effect on the PFC performance was also studied. It was found that increasing the oxygen concentration from 5% to pure oxygen led to the improvement of the maximum power density from 3.5 to 5.2 mW cm^{-2}.

1. Introduction

With the rapid development of society, energy shortage and environmental pollution have become coinstantaneous major issues. Particularly, a large amount of domestic living and industrial wastewater has been disposed into natural water sources, causing serious water pollution [1]. It should be recognized that disposed wastewater is typically rich in organic matters, which contain a significant amount of chemical energy that can meet almost one-third of the global energy demand per year [2]. However, present wastewater treatment technologies mainly focus on degrading organic matters quickly and efficiently. The recovery of the abundant chemical energy contained in disposed wastewater is usually not accounted, leading to huge energy loss [3–4]. Thus the development of a proper technology to recover the chemical energy contained in wastewater to available energy is necessary, which can not only mitigate water contamination problems but also alleviate energy shortage issue.

Photocatalytic fuel cell (PFC) is such a technology, which can degrade wastewater and generate electricity simultaneously. Because of this advantage, it has recently become a new research direction [5–6]. As a key component of PFC, photoanode usually employs semiconductor photocatalysts to photoelectrochemically oxidize the fuel. In this process, the photoanode absorbs photons to create electron-hole pairs. Generated holes then oxidize organic compounds and electrons migrate to the cathode via an external circuit. At the cathode, electrons react with oxygen. As a result, electricity can be generated and organic wastes are degraded into environmentally friendly matter simultaneously. Compared with traditional fuel cells, PFCs possess the following advantages: (1)

* Corresponding author. Tel.: +0086 23 65102474; fax: +0086 23 65102474.
E-mail address: rchen@cqu.edu.cn (R. Chen).

http://dx.doi.org/10.1016/j.electacta.2015.09.090
0013-4686/

PFCs replace the precious metal based anodes with semiconductor photocatalysts, reducing the cost [7]; (2) PFCs can degrade most organic compounds and even actual wastewater through the strong photoelectrochemical oxidizing process, overcoming the fuel type limitation in conventional fuel cells [8]; and (3) the products of PFCs are almost environmentally friendly [5]. Therefore, the PFC is a promising technology for both renewable electricity generation and wastewater treatment.

Currently, most developed PFCs use bare TiO_2 as the photocatalyst, which can only be excited upon UV light [9–11]. These photoanodes are challenging for PFC outdoor applications because the sunlight only contains 4–5% UV light. Therefore, many works have been devoted to develop the solar responsive photocatalyts [12]. In addition, since the PFC can degrade various organic compounds due to strong photocatalytic oxidizability [13–14], numerous efforts have also been devoted to the study of the PFCs degrading different types of wastewater. For example, Li *et al.* investigated the overall PFC performance using phenol as fuel [15]. Seger et al. studied the electrical power production form a PFC using formic acid and other single-carbon organics [16]. However, although some works have been done to test PFCs using different kinds of wastewater, the discharging performance of PFCs with various fuels of single component organics and complex real wastes is still less investigated. In turn, it is still far away from possessing a better understanding of the adaptability of the PFC to various fuel types in real applications.

On the other hand, the electrolyte environment is an important factor influencing the PFC performance. Previous studies on PFCs were usually performed under neutral condition. Nevertheless, the real pH of wastewater is variable. In this case, different reaction and charge transfer mechanisms may be caused, thereby affecting the PFC performance [17–18]. Hence, it is necessary to study the response of the PFC to the electrolyte conditions. Moreover, in conventional PFCs, oxygen usually comes from the oxygen-dissolved electrolyte and the oxygen supply requires additional active oxygen supply equipments [19–20]. The low oxygen solubility in the solution and the energy-consuming oxygen supply equipments limit its practical application. Fortunately, this problem can be well resolved by the design of the air-breathing cathode.

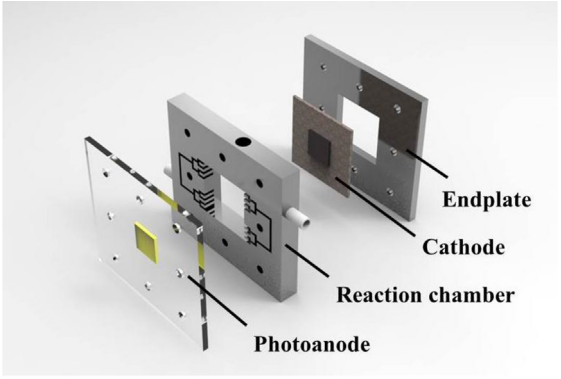
Recently, Wang et al., developed a solar photocatalytic fuel cell using CdS-TiO_2 photoanode and air-breathing cathode for wastewater treatment and simultaneous electricity production [21]. In this study, PFC was enhanced by using CdS quantum-dot-sensitized TiO_2 nanorod array and gas diffusion electrode was employed to improve oxygen reduction reaction at the cathode. However, the PFC was still mainly operated at neutral and acid environments. More recently, Li et al., incorporated optofluidics into the PFC to develop a novel optofluidics based micro photocatalytic fuel cell with eliminating the membrane [22]. In this work, the TiO_2 film was treated by CdS-ZnS to extend the spectral response from UV light to visible light. The air-breathing cathode was employed to handle the mass transfer of oxygen. Because of the incorporation of optofluidics, the intrinsic large surface-to-volume ratio not only shortened the light transport path but also enhanced the mass/charge transport. However, only the effect of the light intensity and fuel concentration was investigated. It can be seen that the air-breathing cathode design were adopted in these two works. The typical oxygen concentration in air is about 21% under most outdoor conditions. However, the oxygen concentration in air may deviate from the average value in some special situations. For example, if a PFC is applied on an airplane, the oxygen concentration in air will drop to only 5% at high altitude. In this case, how the PFC with the air-breathing cathode work at such a low oxygen concentration becomes a problem. Therefore, the effect of the air condition on the performance of the PFC needs to be further investigated.

From the above literature review, it can be known that although the PFC has been widely studied, main efforts are directed to the development of the photocatalysts. Moreover, the most PFCs worked with the membrane at the neutral and oxygen-dissolved cathode. Only a few works on the PFC with a solar responsive photoanode and air-breathing cathode have been reported [21–22]. How such a promising PFC responds to various fuels and electrolytes and air conditions is still unknown. In this work, therefore, we firstly developed a membraneless PFC with a solar responsive photoande and air-breathing cathode. Previous work proved that the composite 75%CdS–25%ZnS are the best choice of a photosensitizer for PFCs running with ethanol or other organic fuels [23]. Therefore, 75%CdS–25%ZnS was incorporated into TiO_2 to form a solar responsive photoanode. An air-breathing cathode was adopted to directly use oxygen in air instead of the dissolved oxygen. With the developed PFC, the performance characteristics under different fuel and electrolyte types and air conditions were systematically characterized to demonstrate its feasibility and adaptability to various environments. The obtained results will provide a guide for operating the PFC towards real applications.

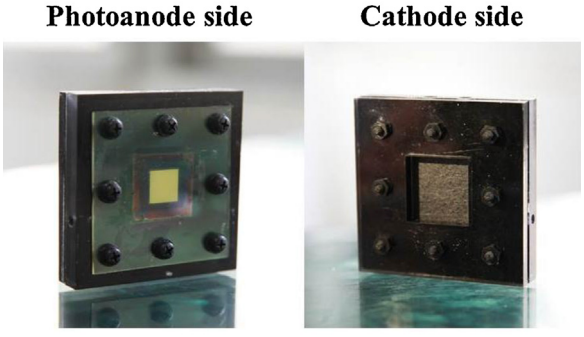
2. Experimental

2.1. Photocatalytic fuel cell

The PFC used in this work is schematically shown in Fig. 1a. A reaction chamber is sandwiched between a photoanode and a cathode. TiO_2 photocatalyst and photosensitizer were sintered on a FTO conducting glass as the photoanode, while the cathode was made by a carbon paper coated with Pt-black nanocatalysts. The active areas of the photoanode and cathode were both 1 cm^2. The



(a)



(b)

Fig. 1. (a) Schematic of the PFC with solar responsive photoanode and air-breathing cathode, (b) Photos of the PFC photoanode and air-breathing cathode.