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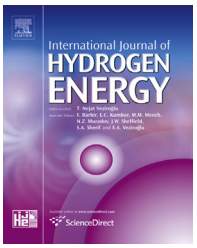

Respective electrode potential characteristics of photocatalytic fuel cell with visible-light responsive photoanode and air-breathing cathode

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ABSTRACT

Photocatalytic fuel cell is a promising technology for simultaneous wastewater treatment and electricity generation. To more directionally improve the cell performance, a deep understanding of respective photoanode and cathode performances is of vital importance. In this work, therefore, a high-performance photocatalytic fuel cell with a visible-light responsive photoanode and an air-breathing cathode was developed to gain insight into each electrode potential characteristics. The potentials of each electrode were measured under different operational parameters. Experimental results showed that too low fuel concentration led to a serious mass transfer limitation at the photoanode and too high fuel concentration led to a low ionic conductivity, both of which deteriorated the cell performance. Therefore, there existed an optimum fuel concentration to achieve the best cell performance. It was also shown that an increase in the electrolyte concentration markedly improved both the photoanode and cathode performances due to enhanced reaction rates and lowered internal resistance, thereby leading to the increased cell performance. In addition, it was demonstrated that the light intensity significantly affected the photoanode potential and increasing the light intensity boosted the cell performance. The results obtained in this work provide the guidance for improving the photocatalytic fuel cell performance in future applications.

Introduction

Every year, a huge amount of wastewater that is one of the main pollutants has been disposed, threatening the human health and drinking water quality. On the other hand, disposed wastewater usually carries numerous organic matters, which can be used for the energy production, like electricity and hydrogen based fuels [1]. Thus, energy recovery from wastewater can not only significantly ease the water

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pollution problem but also contribute to the carbon–neutral energy supply. In recent, photocatalytic fuel cell (PFC), which is an integration of photocatalysis and fuel cell technologies, has emerged [2,3]. This new type of technology can simultaneously degrade the wastewater and generate the electricity, which has shown a promising perspective for sustainable environment and energy development. Typically, a PFC consists of a photoanode, an electrochemical cathode or a photocathode, and a reaction chamber containing fuel and electrolyte. Upon illumination, the photoanode absorbs photons to excite electrons to the conduction band of the semiconductor, creating electron–hole pairs. Subsequently, holes oxidize organic compound at the semiconductor surface, while electrons diffuse through the semiconductor layer and migrate to the cathode via an external circuit, generating the electricity. At the cathode oxygen reacts with coming electrons and ions to complete an oxygen reduction reaction. In this process, the chemical energy stored in organic compounds is converted to electrical energy by utilizing solar energy. Therefore, PFCs realize simultaneous wastewater treatment and electricity production [4–6]. Since the precious metal based anode in conventional fuel cells is replaced by semiconductor photocatalyst, PFCs are much more cost-effective [7]. Moreover, many types of organic wastes can be utilized in PFCs, which overcomes the fuel limitation in conventional fuel cells. Besides, different from traditional microbial fuel cells which exploit living microorganisms as catalysts, the generation of electrons in a PFC system resulting from the photoexcitation process is faster and more direct [8–10], showing superior performance of simultaneous wastewater treatment and electricity production. All these features make PFCs to receive ever-increasing attention all over the world.

As mentioned above, the key components of a PFC include a photoanode, a cathode and a reaction chamber with the electrolyte contained fuel. For the anode, TiO_2 has long been accepted as the photocatalyst due to its high photocatalytic activity and stability. However, bare TiO_2 photocatalyst can only be excited upon UV light (4–5% in the sunlight) [11]. To enhance the visible-light absorption ability of TiO_2, many techniques were proposed [12,13]. Among them, the application of quantum-dots sensitized TiO_2 is promising in harvesting solar energy, because it extends the light absorption range of semiconductor TiO_2 into visible light spectrum and thus increases the sunlight utilization efficiency [14]. For the cathode, Pt based electrocatalysts are usually employed for the oxygen reduction reaction [15]. Oxygen required usually comes from the oxygen-dissolved electrolyte in conventional PFCs. Under such a circumstance, low oxygen solubility in the electrolyte solution greatly limits the cathode performance. Therefore, additional energy-intensive process, such as air-sparging, was required to enhance oxygen transfer to the cathode [16]. An air-breathing cathode (passive supply), which eliminates the gas blower and related auxiliary power consumption, has been proposed. It not only economizes extra energy supply but also makes the system simpler and more compact in comparison to active oxygen supply methods, thus showing high potential for practical application [17,18]. In addition, the electrolyte also plays a significant role in the performance of the PFC, because it determines the ionic conductivity and reaction path and finally affects the cell performance. It has been known that an alkaline electrolyte is more favorable than neural or acid aqueous solution. The reason is that TiO_2 works more efficiently with the presence of OH^- ions, which act as holes scavenger and thus prevent electron–hole recombination and facilitate the oxidation process [19]. In the meantime, the alkaline environment also enhances the oxygen reduction reaction. As a result, a PFC with visible-light responsive photoanode and air-breathing cathode operating with the alkaline electrolyte was developed in this work to improve the cell performance.

In addition to the cell design, the performance of the PFC is also affected by the operational parameters, such as organic waste sorts, fuel concentration, electrolyte conductivity and pH. Numerous efforts have also been devoted to study the effects of the operational parameters [20,21]. Li et al. experimentally investigated the overall PFC performance in phenol solution under various levels of electrolyte concentrations [22]. Antoniadou and Lianos evaluated the performance of the electricity generation in a photoactivated fuel cell with different common wastes, such as glycerol, xylitol and sorbitol and studied the overall system performance [23]. Li and Xu et al. studied the effects of pH on the performance of the electricity generation and organic compound degradation in a PFC [24]. However, these previous works mainly focused on the overall discharging performance of the PFC. It should be noted that as for PFCs, the cell performance depends on both the photoanode and cathode potentials, which independently vary with the operational parameters. In this case, the improvement in the overall cell performance requires a deep insight into respective photoanode and cathode performances, with which the strategies to improve the cell performance can be more directional. However, it is still far away from possessing a solid scientific understanding of respective photoanode and cathode discharging characteristics. Therefore, the goal of this work is to develop a high performance PFC with the visible-light responsive photoanode, air-breathing cathode and alkaline electrolyte, by which respective potentials of the photoanode and cathode were studied. Particular attention was paid to studying respective characteristics of the photoanode and cathode under different fuel concentrations, electrolyte concentrations and light intensities. With this fundamental research, the PFC performance could be eventually optimized and its application prospects would be broadened.

Experimental

Description of photocatalytic fuel cell

Fig. 1a shows the schematic illustration of the PFC applied in the present study. As shown, the PFC consisted of a photoanode, a reaction chamber and a cathode and these components were stacked in a sandwiched structure. Two endplates were placed to fix the cell structure with bolts. Both the endplates had a window for the illumination at the photoanode and breathing air at the cathode, respectively. The photoanode was manufactured by a FTO conducting glass coated with TiO_2 photocatalyst and photosensitizer. The cathode was

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