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Generation of hydrogen free radicals from water for fuels by electric field induction

Guangzai Nong *, Yiyi Chen, Ming Li, Zongwen Zhou

Center for Sugar Engineering and Technology Research, Guangxi University, Nanning, Guangxi 530004, PR China

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ABSTRACT

Water is the most abundant resource for generating hydrogen fuel. In addition to dissociating H^+ and ^-OH ions, certain water molecules dissociate to radicals under an electric field are considered. Therefore, an electric field inducing reactor is constructed and operated to generate hydrogen free radicals in this paper. Hydrogen free radicals begin to be generated under a 1.0 V electric field, and increasing the voltage and temperature increases the number of hydrogen free radicals. The production rate of hydrogen free radicals is 0.245 mmol/(L h) at 5.0 V and room temperature. The generated hydrogen free radicals are converted to polymer fuel and hydrogen fuel at production rates of 0.0093 mmol/(L h) and 0.0038 mmol/(L h) respectively, under 5.0 V and 0.25 mA. The results provide a way to generate hydrogen free radicals, which might be used to generate hydrocarbon fuel in industrial manufacture.

1. Introduction

Water covers 71% of the Earth's surface and is one of the most abundant resources [1–3]. Because water contains 11.1% in mass of the hydrogen element, it is considered as an abundant resource to generate hydrogen fuel [4–6]. Water splitting for hydrogen fuel can be achieved by electrolysis [7–9], in which the electrical energy consumption for hydrogen fuel commonly exceeds 45.0 kW h per kilogram; up to 26.5 kW h per kilogram can be saved after titanic nanotubes are used [10]. The energy efficiency is 92.0% for electrolysis of wastewater containing anaerobic sludge [11].

The mechanisms of water splitting by electrolysis can be described as some of water molecules are dissociated to H^+ and ^-OH ions. Each of the H^+ accepts one electron from the cathode plate and becomes a hydrogen atom on the surface of the cathode plate by electrolysis. Those generated hydrogen atom temporarily exist in the form of M – H. Subsequent reactions between M – H and M – H (or H_3O^+) occur and generate hydrogen fuels [12–14].

$$H_2O \rightarrow H^+ + {}^-OH \quad (1)$$

$$H_2O + H^+ \rightarrow H_3O^+ \quad (2)$$

$$H_3O^+ + e^- + M \rightarrow M - H + H_2O \quad (\text{Volmer}) \quad (3)$$

$$M - H + M - H \rightarrow 2M + H_2 \quad (\text{Tafel}) \quad (4)$$

$$M - H + H_3O^+ + e^- \rightarrow M + H_2 + H_2O \quad (\text{Heyrovsky}) \quad (5)$$

Water splitting for hydrogen fuels can also be achieved by photocatalytic methods utilizing sunlight [15–17]. Jacobsson et al. achieved an energy efficiency of (hydrogen/solar) over 10.0% [18], which is the highest value reported. The mechanisms of water splitting by photocatalytic methods can be described as follows: the photons irradiate a catalyst powder to activate the electrons from the basic orbital to the active orbital of the molecules or crystals, generating free electrons and holes. Then, the free electrons are donated to the H^+ in water, generating hydrogen gas, and the holes accept electrons from the hydroxide ions in the water, generating oxygen gas [19–23].

$$H_2O \rightarrow H^+ + {}^-OH \quad (1)$$

$$h\nu + \text{Catalyst} \rightarrow \text{Catalyst} + e^- + h^+ \quad (6)$$

$$4{}^-OH + 4h^+ \rightarrow 2H_2O + O_2 \uparrow \quad (7)$$

$$4H^+ + 4e^- \rightarrow 2H_2 \uparrow \quad (8)$$

As mentioned previously, water dissociated to H^+ and ^-OH is the first step to generating hydrogen fuel. In addition to dissociating to H^+ and ^-OH ions, certain water molecules that directly dissociated to hydrogen free radicals and hydroxyl free radicals under an electric field are considered as following.

* Corresponding author. Tel.: +86 0771 3272232; fax: +86 0771 3231590.
E-mail address: gz.nonginguilin@163.com (G. Nong).

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There are two O–H bonds in a water molecule. The space of the O–H bond can be divided into three parts: the S space (S orbital near the hydrogen nuclei), the Bonding space (overlapping space) and P space (P orbital near to the oxygen nuclei), shown as Fig. 1(a). When the two bonding electrons appears in the bonding space, water would be presented in the common style (H–O–H), as shown in Fig. 1(a). When the two bonding electrons appears in the P space, there is not electron occupying the bonding space, and therefore, the bond would be temporarily broken, generating a hydrogen ion and hydroxide ion, so water would be presented in the ion style ($H^+(O–H)^-$), as shown in Fig. 1(b). When the one bonding electron appears in the S space, and at the same time, another bonding electron appears in the P space, there is no electron occupying the bonding space. Therefore, the bond would be temporarily broken, generating hydrogen radicals and hydroxyl radicals, so water would be presented in the radical style (·H (·O–H)), as shown in Fig. 1(c).

In general, because the distance between those radicals is very short, the generated hydrogen radicals and hydroxyl radicals combine swiftly, i.e., in the time it takes the electrons to return to occupying the bonding space. To combine swiftly, those generated free radicals cannot leave the space of the water molecule, so they would be not truly free radicals. While under an electric field, the electric field force might cause a directional rotation of the hydroxyl free radical, which might lead to the separation of the hydrogen free radical and hydroxyl free radical, and generates true free radicals, as shown in Fig. 1(d).

Based on the consideration, an electric inducing reactor is constructed and used to generate hydrogen free radicals, and then the generated hydrogen free radicals are converted to fuel. The results provide a way to generate hydrogen free radicals from water and, at the same time, provide a new way for hydrocarbon fuel generation.

2. Experimental

2.1. Construction of an electric field inducing reactor

Based on the consideration mentioned ahead, an electric field inducing reactor is constructed to generate hydrogen free radicals, as shown in Fig. 1. The reaction space was separated into a cathode chamber, a free space and an anode chamber by sealing with a cationic exchange membrane. Only the free radicals generated in the free space were captured and determined. The free radicals generated on the surfaces of the plates were not collected. This design helps obtain direct evidence that the captured free radicals are generated in the free space and not generated on the surface of the electric plates.

The hydrogen free radicals and hydrogen generated in the free space were investigated in two experiments, respectively. Working in conditions of 5.0 V, 0.25 mA and 48 h, the results of hydrogen free radicals captured by CO_2 are shown in Table 1, and the results of hydrogen gas generated are shown in Table 2 (see Fig. 2).

2.2. Methods to capture and calculate the hydrogen free radicals

The hydrogen free radicals are captured by CO_2, generating oxalates and polymers [24]. The CO_2 gas was conducted into the free space, where the generated hydrogen free radicals were captured. Based on the captured reactions, the total reaction number of the hydrogen free radicals ($N_{H,r}$) is the sum of two times the number of oxalate molecules ($N_{u,oxalate}$) and 26 times the number of units of the polymer ($N_{u,polymer}$).

$$N_{H,r} = 2 \times N_{u,oxalate} + 26 \times N_{u,polymer} \quad (9)$$

The reactions of hydrogen free radicals captured by CO_2 have been described in our previous paper. The oxalate generation reaction is described as Eq. (10); and combining the equations yields the total Eq. (11) of the polymers generation.

$$2H + 2CO_2 \rightarrow H_2C_2O_4 \quad (10)$$

$$26nH + 8nCO_2 \rightarrow H(OCOCOOCH_2CH_2OCOCH(OH)OCH_2CH_2)_nOH + (8n-1)H_2O \quad (11)$$

Table 1
Results of hydrogen free radicals captured in the free space (5.0 V, 0.25 mA, 48 h).

Products	Molecules	Masses, mg	·H captured, mmol	$R_{p,H}$, mmol/(L h)
Polymers	$(C_8H_{10}O_8)_n$	102.5	11.39	0.237
Oxalates	$H_2C_2O_4$	17.9	0.40	0.008
Total			11.79	0.245

Table 2
Results of hydrogen gas generated in the free space (5 V, 0.25 mA, 48 h).

Products	Volume, ml	$R_{p,H2,}$ mmol/(L h)
H_2	4.1	0.0038

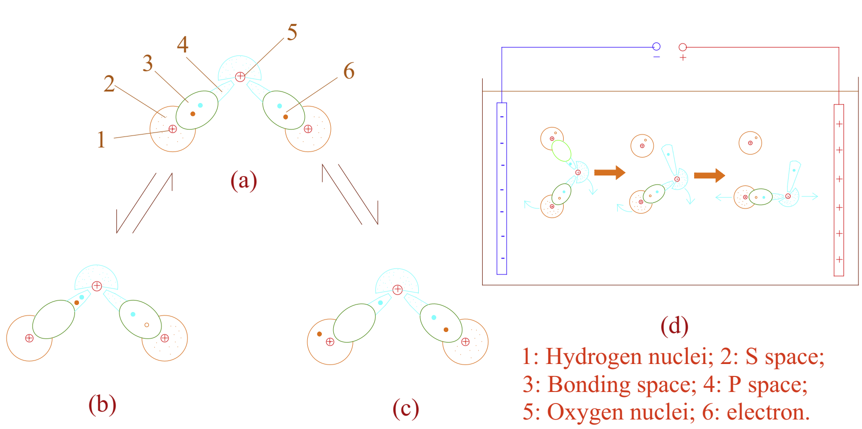

Fig. 1. Consideration of water splitting to radicals under an electric field.