Energy 131 (2017) 98–105

Contents lists available at ScienceDirect

Energy

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

Facile hydrogen production from Al-water reaction promoted by choline hydroxide

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ARTICLE INFO

Article history:
Received 8 June 2016
Received in revised form
8 April 2017
Accepted 5 May 2017
Available online 6 May 2017

Keywords:
Hydrogen production
Al-water reaction
Choline hydroxide
Fuel cell

ABSTRACT

Choline hydroxide was used to accelerate the Al-water reaction to produce hydrogen efficiently and steadily, with only water and aluminum consumption. The effects of parameters such as initial aluminum mass, alkali concentration and temperature on the reaction rate and yield were studied. Compared with the average value 52.55 kJ/mol of other activation methods, the apparent activation energy of 45.92 kJ/mol indicates that choline hydroxide can promote the reaction significantly. The mechanism analysis demonstrates that the dissociation equilibrium of choline hydroxide ($pK_b = 1.3$) can restrict the complete dissociation in the initial reaction stage and accelerate the regeneration of OH^- in the latter stage. Compared with the NaOH ($pK_b = 0.2$) under the same condition, the choline hydroxide is less corrosive. The dissociation equilibrium of choline hydroxide was also verified by the HSAB theory. The average hydrogen generation rate activated by choline hydroxide is as fast as that of NaOH. The standard deviation of hydrogen generation rate of choline hydroxide is 78.7 mL/min, lower than that of NaOH being 108.3 mL/min, indicating the stability by choline hydroxide. Therefore, the application of choline hydroxide can produce hydrogen for fuel cells due to its weak corrosion and stable supplement of OH^-.

1. Introduction

Hydrogen is the most promising and appropriate energy carrier, which can substitute the non-sustainable fossil fuel and can be used in stationary or portable fuel cells to generate electricity due to its environmental friendliness and high calorific value. There are many methods to produce hydrogen, such as the steam reforming of natural gas, electrolysis of water and reaction of chemical hydride [1]. However, the steam reforming of natural gas still depletes the fossil fuel and the water electrolysis is restricted by its high cost. Besides, the difficulties of hydrogen storage and transport still hinder the application of this clean fuel. In-situ hydrogen production is attracting much more attention for its application in power source. Despite sodium borohydride ($NaBH_4$) is safe and efficient enough to produce hydrogen in situ, the expensive raw materials of hydrides and the susceptibility to moist in the air also limits its application [2,3].

Production of hydrogen by the reaction of Al-water is promising for its mild reaction conditions and cheap raw material which is also recyclable [4]. However, the reaction is always hindered by the oxide film formed on the aluminum surface through preventing the water contact with the activated aluminum. The activation methods mainly fall into two categories, that is, the treatment of aluminum metal and the improvement of reaction medium.

The treatment of aluminum metal includes amalgamation by mercury, surface treatment with metal gallium [5] and milling with hydrides [6]. Though these treatments to the aluminum can accelerate the reaction kinetics, the adulteration of other elements may make it difficult to recycle the aluminum metal. Another modification method is to improve the purity of the aluminum metal to enhance the reaction kinetics [7] and ensure the purity of hydrogen supplied to the hydrogen fuel cell [1]. The high-purity aluminum is featured with the theoretically best gravimetric capacity and volumetric capacity [8]. Wang et al. [9] have found that pure aluminum reacts much easier with inorganic alkali solution than the Al-Si alloy. The high-purity aluminum can also be regenerated through the three-layer electrolysis technique from the byproduct [5]. The advancement of high-purity preparation

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http://dx.doi.org/10.1016/j.energy.2017.05.031
0360-5442/

methods such as zone refining ensures the economical efficiency of the application of high-purity aluminum [10]. Besides, the aluminum can be regenerated easily due to the absence of other metal elements like sodium or calcium. Based on the features of high-purity aluminum, it was used in this study to generate hydrogen.

On the other hand, changing the reaction medium can also enhance the Al-water reaction, such as the reaction of aluminum with cobalt (II) chloride solution [11] or aqueous alkali medium [12–15]. Both the type of alkali and the composition of aluminum can influence the hydrogen generation rate. Soler et al. [16] have investigated the effects of various inorganic alkalis on the reaction, including NaOH, KOH and $Ca(OH)_2$. However, NaOH and KOH are too corrosive for the hydrogen generation apparatus and usually lead the reaction to an uncontrolled state, especially in the initial reaction stage [17]. The stability of hydrogen generation is essential for the application to fuel cells [18,19]. There has been some work to lower the basicity or substitute NaOH, such as the application of oxometallates [20–22] and calcium hydroxide [14]. These works concentrate on the change of the cations in alkali medium. Halaša et al. [15] found that the aggressiveness of a given hydroxide is significantly influenced by the cation present in the solution even though it does not directly participate in the reaction. For the inorganic bases, the alkalinity is related to the solubility whereas the alkalinity of organic bases is influenced by many factors such as inductive, electrostatic and electro-delocalization effects [23]. Some organic alkalis solution cannot dissolve the aluminum even though they are featured with high pH value [24]. The dissociation rate and its balance of aluminate intermediates are crucial for the Al-water reaction rate. Choline hydroxide is a quaternary ammonium salt and widely used as basic catalyst [25] and structure-directing agent [26]. Zhu et al. [27] synthesized the biscoumarin using the choline hydroxide as an efficient and green catalyst which is cheap and reusable. The choline ion is green and safe for the environment because it can be decomposed both physiologically and environmentally [28–30]. But little work has been done to produce hydrogen by activating Al-water reaction with organic alkali.

The main objective of this study is to illustrate the feasibility of choline hydroxide to accelerate the Al-water reaction to produce hydrogen in a relatively stable rate from the aspect of average hydrogen generation rate, thus providing a steady and efficient way to produce hydrogen for fuel cell. The application of choline hydroxide can eliminate the passivation of the oxide or hydroxide film to speed up the Al-water reaction significantly and overcome the corrosion problem of strong inorganic alkali. The reaction kinetics and mechanism were investigated here to provide a thorough understanding of the role of the organic alkali – chloride hydroxide.

2. Experimental

2.1. Chemicals

High-purity aluminum (purity >99.999%) is supplied by Xinjiang Joinworld Company and processed into the flake shape. The aluminum oxide film is formed in nature by contacting with air under ambient temperature and its mass fraction in the Al flakes is estimated to be 38.6–77.3 ppm. All aluminum was exposed to air when added to the solution. NaOH (GR) is provided by Xilong Chemical Co. and the choline hydroxide (Chemical formula: $C_5H_{14}NO^+$ OH^-, 35% solution on dry basis) is provided by Jinan Jinhui Chemical Co, where the function group $C_5H_{14}NO^+$ of choline hydroxide is denoted as R^+ and the choline hydroxide is written as ROH in the following for simplification. High-purity water of 18 MΩ was used. All reagents were used as received.

2.2. Experiment equipment

The reaction system used in the present work is schematically demonstrated in Fig. 1. The reactor is a jacketed glass vessel of 1 L volume. The temperature is monitored with a Pt100 sensor and kept by a thermostat with precision of ±0.01 °C. The hydrogen generation rate is measured by a D07-19BM Mass Flow Meters (Beijng Sevenstar, China) with a measurement range being 0–800 mL/min and the error range being ±1% (±8 mL/min). All the transient information was collected and conveyed to the computer.

The alkali solution composed of choline hydroxide and water was poured to the reactor and the stirrer speed was set to 400 rpm to ensure homogeneous suspension. The total volume of the alkali solution was kept constant of 500 mL in all experiments. When the temperature reached a certain value, the aluminum flakes were added into the reactor quickly and the reaction started spontaneously. The online temperature change and transient gas flow were recorded at the same time.

2.3. Characterization

The hydrogen yield is defined as the ratio of produced hydrogen volume to the theoretical value of 1245 mL hydrogen/g Al. The morphology of the aluminum flakes was characterized by the SEM (JSM-6700F). The XPS analyses were performed on ECSALAB 250xi (Thermo Fisher Scientific) with an Al-K Alpha source type. The pH of the alkali solution was measured with pH meter (SevenExcellence Multiparameter, Mettler Toledo).

3. Results and discussion

3.1. Hydrogen generation kinetics

The hydrogen generation rate from Al-water reaction promoted by ROH can be influenced by the alkali concentration, reaction temperature and initial aluminum mass. First, a set of experiments were conducted to investigate the impact of ROH concentration on the hydrogen generation rate in the present study. 20 g/L aluminum reacts with different alkali concentrations under 90 °C. As shown in Fig. 2, the reaction rate during the initial reaction stage increases with the increase of initial alkali concentration. The maximum hydrogen generation rates of several ROH concentrations (0.5595, 0.2798, 0.1398 and 0.0936 mol/L) correspond to 732.6, 509.4, 394.7 and 268 mL/min and the reaction order with respect to alkali concentration of 1 is estimated in the initial reaction stage (before

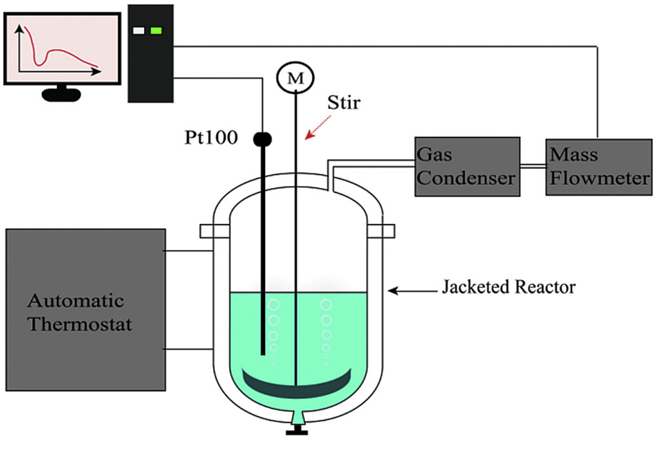

Fig. 1. Experiment setup for aluminum-water reaction.