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The effect of various factors on the hydrogen generation by hydrolysis reaction of potassium borohydride

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Abstract

Potassium borohydride (KBH_4) reacted very slowly with water to liberate 4 mol of hydrogen/mol of compound at room temperature. The hydrolysis and stability conditions of KBH_4 investigated depend on KBH_4 concentrations, concentration of alkaline solutions, temperatures and electrical field intensity. Yield of produced hydrogen by self-hydrolysis of KBH_4 increases as the temperature increased and it produced 53.9% yield at the end of 300 min at 60 °C. The reaction rate order of hydrolysis of KBH_4 in aqueous solution is found at about 0.7–0.8 and the activation energy for hydrolysis is calculated as 14,700 kJ/mol. Potassium borohydride is stable both in room temperature and in aqueous alkaline solution. In this study, the electrical field that is not needed for catalytic activity was used for the hydrolysis of KBH_4 aqueous solution. It was found that 6 mol of hydrogen/mol of potassium borohydride was liberated in the presence of electrical field, whereas 4 mol of hydrogen was produced in the absence of electrical field per mol of potassium borohydride.

Keywords: Potassium borohydride; Hydrogen generation; Electrical field; Activation energy

1. Introduction

A fuel cell actuated with hydrogen (H_2) and oxygen (O_2) has been under development in order to overcome the problems of energy and environment in future. The energy obtained from a reaction of H_2 and O_2 is directly converted into electric energy. Since a fuel cell has an efficiency much higher than that of conventional combustion engines, fuel cell vehicle (FCV) is expected to be a vehicle having high efficiency [1,2]. A proton exchange membrane fuel cell (PEMFC) is the prime power source for FCV, as well as another application called a fuel cell uninterrupted power supply (FCUPS). The uninterrupted or emergency power system for a FCUPS system currently combines a battery and a diesel generator. But a PEFC system has the potential to be a future power system for emergency FCUPS. In order to fuel the FCV or FCUPS, a source of proton is required for the electrochemical reaction. One of the most widely envisioned sources of fuel of FCV or FCUPS is H_2. Therefore, it is necessary to have a storage tank of H_2 to start the system on demand.

Hydrogen can be stored in tanks of compressed [2,3] or liquefied H_2 [3] or by adsorption on activated carbon [4], carbon nanotubes [3–6] and graphite nanofiber [7,8] or in a hydrogen-adsorbing alloy [9] or a chemical hydride such as NaH [10], LiH [11], $NaAlH_4$ [12] or Sodiumborohydride ($NaBH_4$) [13,14].

Among these methods, attention has recently been given to the hydrolysis of chemical hydride (ionic hydride) such as NaH [10], LiH [11] and $NaBH_4$ [13,14]. NaH and LiH vigorously react with water. Therefore, NaH is coated with a resin film and the film is cut to generate hydrogen in the presence of water on demand [10]. LiH is prepared as a slurry with light mineral oil and the dispersion has been found to be stable for a long period of time at normal temperature and pressure [11].

A rather simple way to produce hydrogen is based on the dehydrogenation of light weight metallic or nonmetallic hydrides. The catalytic dehydrogenation of sodium tetra hydroaluminate ($NaAlH_4$) has been recently reported to liberate ∼ 7 wt% hydrogen at a moderate temperature of about 70 °C [15]. However, since this type of hydride is very sensitive to

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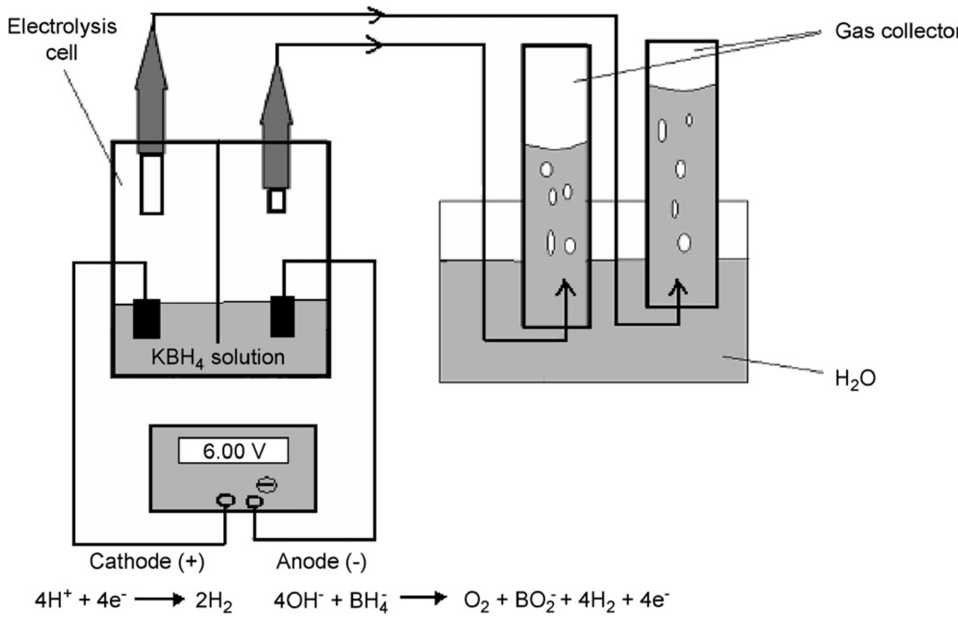

Fig. 1. Electrolysis system.

environmental moisture or oxygen, safety problems may hinder their practical use [16].

Aqueous borohydride seems to be an ideal hydrogen source because it is stable under ordinary conditions and liberates hydrogen in a safe and controllable way. The first investigation of BH_4^- hydrolysis was reported in the early 1950s by Schlesinger et al. [13], who extensively and qualitatively studied the accelerating effects of acids and transition metal salts on the rate of BH_4^- hydrolysis.

$NaBH_4$ is stable compared to other chemical hydrides and is easy to handle [13,14]. At room temperatures, only a small percentage of the theoretical amount of H_2 is liberated by hydrolysis reaction of $NaBH_4$ and H_2O [17], but the hydrolysis is accelerated by the use of catalysts [13–19]. $NaBH_4$ and potassium borohydride (KBH_4) are safe and practical means of storing hydrogen, but both of them are sensitive to moisture in the air in the solid state [20]. Similar to $NaBH_4$, KBH_4 can be used to reduce aldehydes, ketones, acid chlorides and anhydrides. It is also used in vitamin A synthesis and as a fuel for a fuel cell due to its high reactivity, high hydrogen content and high potential [21]. KBH_4 is usually synthesized by a reaction of $NaBH_4$ with KOH [22]. Also, KBH_4 can be prepared through a mechano-chemical reaction at room temperature by using saline hydrides and dehydrated borates [23].

Although many studies have been done by a lot of researchers on the hydrolysis of sodium and lithiumborohydride [13–20,24], we have not noticed any study on the hydrolysis of KBH_4. In view of such circumstance, the hydrolysis of KBH_4 is of interest for the generation of H_2 because KBH_4 has hydrogen content such as $LiBH_4$ [24] and $NaBH_4$ [14]. Thus, the main aim of this study is to determine the hydrolysis behaviour of KBH_4 at different conditions such as temperature, pH and electrical field.

2. Experimental

KBH_4 (Merck; molecular weight: 53.94 g/mol, assay ⩾ 97%) was used for the reaction with water. The solubility of KBH_4 in water at 25°C is 190 g/L of water. It slowly adsorbs water from moist air to form hydride which decomposes slowly to form hydrogen and potassium metaborate. The effect of different percentages of NaOH and KOH were used in the experiments in order to maintain the stability of KBH_4 solution.

The effect of electrical field on the hydrolysis of KBH_4 was carried out by applying a certain amount of voltage (6–8 V) between two parallel platinium plates as shown in Fig. 1. The distance between the two parallel plates used was 2 cm. An electrolysis cell having two different gas outlets was used in the experiment (Fig. 1). The outlet gas in both anode and cathode sections was collected and measured by using a water trap separately.

The amounts of H_2 generation in our experiments were determined depending on different factors as follows. Various KBH_4 percentages (5–20%) of aqueous solutions were prepared by adding different amounts of KBH_4 (200–1000 mg KBH_4) into an Erlenmayer flask having a volume of 50 mL. The thermal hydrolysis of KBH_4 in aqueous solution was studied at a temperature range of 20–60 °C in the waterbath with temperature sensitivity of 0.1 °C. The generated H_2 gas was collected and its volume was measured in a water trap during the reaction of KBH_4 with water simultaneously. A measured volume of released gas was subsequently converted into yield of produced H_2 after the total amount of gas had been collected.

The crystallization of KBH_4 in solution with the initial percentage of 20% was realized both in the pure state and with the presence of 2% KOH by slow evaporation at room temperature.