Selection of reagent ratio for hydrogen production via Al nanopowder oxidation

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Abstract. In the present paper, Al is considered as a basic material for hydrogen production from water because of its high performance, availability, and environmental safety of its reaction products. Here we report the results of experimental trials on the oxidation of Alex-grade Al nanopowder by water when heated and stirred. The plots of pressure and temperature versus Al oxidation time in a high-pressure reactor are given. We show the advantages of hydrogen extraction from hydrogen-containing materials via the oxidation of metal powders. An optimum mass ratio of Al nanopowder to water at which the oxidation reaction takes place to release hydrogen has been identified by varying the reagent ratio. It can be concluded at this point of the study that it is advisable to maintain the \( \text{H}_2\text{O}\)-to-Al nanopowder ratio of 11:1 for hydrogen production. Hydrogen resulted from this reaction can be used to supply small-scale power packs based on hydrogen FC.

1. Introduction

The development of technologies that allow the replacement of conventional power sources of portable electronics is well-known to be an important challenge in Russia and worldwide. There is an urgent demand to implement renewable and clean fuel alternatives to satisfy the energetic demand of the 21st century due to fossil fuel depletion and to the importance of reducing emissions of greenhouse and polluting gases, responsible of harmful effects like the climate change. The use of hydrogen as an energy carrier has extensively been discussed over the past decades. The conventional small batteries and accumulator batteries do not always now meet the demands of portable electrical appliances and, besides, they are self-discharging over time. The utilization of hydrogen as an energy carrier offers a range of advantages among which are a high energy capacity of 121 kJ/g per mass unit and absent toxic by-products when burnt (or oxidized) [1]. There now exist developments on using hydrogen as fuel additives in ordinary internal combustion engines to improve the engine performance and as the basic fuel component in air-hydrogen FCs. This is attributed to the environmental friendliness of hydrogen because the only by-product of its oxidation is water; besides, in the case of a great leakage of hydrogen, it does not accumulate in the atmosphere and escapes beyond the stratosphere [2, 3]. In this regard, the development of new energy supply sources based on hydrogen is a highly relevant challenge of today.

The present paper aimed to select and quantify the optimum ratio of components for hydrogen production. By using a lab-scale setup based on a high-pressure reactor to determine the component ratio, experimental trials on the oxidation of Al nanopowder by water were done.
The present paper will mainly describe and discuss the reaction of powdered Al with water in a reactor rigged with vigorous stirring and initiating heat-up. The paper is structured as follows: the relevance of this work is stated in section 1; FC technologies are discussed in section 2; the characteristics of the primary components used in the experiments are summarized in section 3; the experiment of the oxidation of the Al nanopowders and selection of the reagent ratio for hydrogen production is stated in section 4. Section 5 presented the conclusions derived from the results of the study.

2. Theoretical Investigation

Being the most eco-benign energy carrier, hydrogen can be utilized as a fuel in FCs (Fig. 1) that are devices transforming chemical energy stored in hydrogen into the electrical.

![Figure 1. A general schematic of the FC.](image)

The FC represents an electrochemical source of current capable of transforming chemical energy into the electrical from constantly coming active agents during the electrochemical processes. For the energy generation, the FC utilizes hydrogen as a fuel, and oxygen as an oxidizer, which are stored outside the FC and supplied as they are consumed. Therefore, such a device can theoretically operate continuously until the supply of active agents stops. A single FC consists of an electrolyte sandwiched between two thin electrodes (a porous anode and cathode). Hydrogen is fed to the anode where a catalyst separates hydrogen's negatively charged electrons from positively charged ions (protons). At the cathode, oxygen combines with electrons and protons resulting in water. The electrons from the anode side of the cell cannot pass through the membrane to the cathode; they must travel around it across an electrical circuit to reach the other side of the cell. This movement of electrons is an electrical current.

Among all the advantages of using such power sources, the main difficulty involves the organization of timely and continuous supply of fuel to FC. Since the storage and transportation of hydrogen in cylinders under pressure is difficult due to the high penetrating power of its molecules, it would be convenient to generate hydrogen directly in situ consumption.

The amount of power produced by a FC depends upon several factors, such as FC type, cell size, the temperature at which it operates, and the pressure at which the gases are supplied to the cell. The most prominent type FCs are: proton exchange membrane (or solid polymer), alkaline, phosphoric acid (this is low-temperature FCs), molten carbonate, solid oxide (high-temperature FCs). Depending on the type, the FC can use not only pure hydrogen as the fuel, but also hydrogen-bearing compounds such as methanol, natural gas, etc. Moreover, these devices exhibit a high efficiency factor of 50–80%, environmental friendliness, and a high energy capacity.
The prototypes of portable hydrogen-based energy supply sources, which could further replace conventional small batteries and accumulator batteries, were discussed [4, 5]. The main difficulty dealing with hydrogen is its storage and transportation, since its molecules exhibit a high penetrability and the transportation of hydrogen gas in high-pressure cylinders is not safe; the more so, this is not completely befitting for supplying small-scale portable energy sources. The difficulties in storing and handling can be avoided if hydrogen is produced from available and safe raw materials at the place of its consumption. A number of studies [6–8] corroborate the promising outlook of using decomposition of water by hydroreactive alloys as a hydrogen production method to supply autonomous energy sources. Such systems are quite compact and require no supplementary energy sources.

Aluminum is viewed as the key material for hydrogen generation from water because of its high performance, availability, and environmental safety of the reaction products. Aluminum powders under normal conditions are always coated with a thin, solid, oxide film which prevents them from oxygen exposure. If the film integrity is damaged, Al begins to react with water to liberate hydrogen. To break down the oxide film, various techniques are employed, among which are the mechanical activation of powder and the use of different additives that activate the powder or destroy the oxide film [9].

Of special interest are submicron and nano-sized Al powders because they possess a range of properties distinct from those of compact metal and coarse industrial powders. It is essential to determine the ratios of starting components at which the Al oxidation reaction takes place actively to release a large quantity of hydrogen.

As is well-known, many metals when reacted with water and aqueous solutions are oxidized to give off hydrogen [10]. Al nanopowder is among the key materials for hydrogen generation because of its availability, safety of reaction by-products, and efficiency. The oxidation reaction of the metallic Al is heterogeneous and exothermic. The Al oxidation process follows the reaction:

$$2Al + 3H_2O = Al(OH)_3 + 1.5H_2.$$  

As per the stoichiometric estimations, the oxidation of 1 g Al by water liberates 1.24 L hydrogen and Al hydroxide which can be processed further on. Thus, the hydrogen generation by this technique may avoid the problems of its storage and transportation to the place of use, as well as ensure a timely and continuous supply of fuel to an autonomous device of energy generation based on hydrogen FCs.

3. Materials and methods

To quantify the optimum reagent ratio for obtaining a hydrogen fuel, experimental trials were done to oxidize Al powder by water. Since nano-sized powders are dissimilar in properties to coarse industrial powders having a higher reactivity, here we used Alex-grade Al nanopowder derived by the electroexplosion of wire under argon [11].

Because the properties of powders undergo changes over time, we measured the particle size of the powders prior to experiments and measured the content of active Al from the released hydrogen amount via volumetry before and after their oxidation by water. The characteristics of Alex nanopowder, which was employed in the experimental trials, are summarized in Table 1.

| Table 1. Characteristics of Alex nanopowder. |
|----------------|----------------|----------------|----------------|
| Powder grade | Mean particle size, µm | Content of active Al, % | Content of active Al in reaction products, % |
| Alex | 0.12 – 0.18 | 79.5 | 0.66 |

The content of active Al was measured by the indirect technique, that is, by quantifying the hydrogen volume resulted from the reaction between Al and sodium hydroxide (GOST 5494-95 Pudra Aluminievaya). As is seen in Table 1, the content of active Al can determine how completely the powder has reacted [12, 13].
The particle size of the Al powders was measured by the PIP 8.1/9.0 optical analyzer. Figures 2, 3 display a microphotograph of the Al powder, and a histogram of the probability-density function of the particle-size distribution.

![Microphotograph of Al powder](image)

**Figure 2.** A microphotograph of the Al particles: scale spacing: 29.16 µm

![Histogram of particle size distribution](image)

**Figure 3.** A microphotograph of the Al particles and particle-size distribution function of Al powder (data acquired by an OLYMPUS OMEC DC130 optical analyzer).

According to the preliminary experiments [14], the oxidation of 1 g Al furnishes 1.24 L hydrogen (0°C at 1 atm). At a stoichiometric ratio, the complete oxidation of 27 g (1 mol) Al requires 54 g (i.e. 3 mol) water, that is, the minimum estimated ratio of nanopowder to water is 1 to 2. Because this reaction is exothermic, the mixture temperature rises intensively as a result of the reaction, and the Al oxidation may require additional water to avoid the powder sintering due to water evaporation during the reaction. Therefore, the experiments used excess water, particularly 100 g for oxidation of 1, 5 and 9 g Al nanopowder.

The oxidation of Al powder by water was carried out in a Top Industrie autoclave [15] consisting of a high-pressure reactor with a magnetic stirrer (Figure 4 (a)) and a control unit (Figure 4 (b)).
The control unit enables recording the changes in pressure and temperature values as the reaction proceeds.

4. Results and discussion

We tested samples of aqueous suspensions with different mass ratios of reagents, i.e. the Al nanopowder-to-water ratios of 1:100, 1:20 and 1:11. Since the passivating oxide coating is always present on the Al surface, the suspension being continuously stirred in the reactor was heated up to 60°C to initiate the reaction, and once the reactor pressure began to grow, the stirring was continued without heating. The plots of the reactor pressure and temperature versus time are depicted in Figures 5, 6.
Figure 6. Plots of pressure in the reactor versus time (curve 1 is the 1:100 mass ratio of Al nanopowder to H$_2$O; curve 2 is the 1:20 mass ratio of Al nanopowder to H$_2$O; and curve 3 is the 1:11 mass ratio of Al nanopowder to H$_2$O).

The sample with an Al nanopowder-to-H$_2$O mass ratio of 1:11 (Figure 5, curve 3) showed self-heating of the particles at 25 min after the heat-up was disabled. At a greater water content, the oxidation of Al was slower with a slight temperature increment after the heat-up was turned off (Figure 5, curve 2). The self-heating of the suspension was not observed when 1 g Al nanopowder was oxidized by 100 g water (Figure 5, curve 1), with the reactor pressure changing slightly (Figure 6, curve 1).

5. Conclusions
To sum up, experimental trials were done to oxidize Al nanopowder by water. The following conclusions can be made from the analysis of the obtained data:

1. The oxidation of Al nanopowder in water exhibits an induction period which shortens as the Al concentration in water increases. Thus, an increase in the Al nanopowder concentration in water accelerates the Al oxidation reaction progress.

2. It can be concluded at this point of the study that it is advisable to maintain the H$_2$O-to-Al nanopowder ratio of 11:1 for hydrogen production when designing a hydrogen-based energy source.

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Appendices
Al – aluminium
FC – fuel cell

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