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Cobalt–iron–boron catalyst-induced aluminum–water reaction

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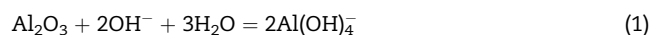
ABSTRACT

Hydrogen generation based on the corrosion of aluminum has been evaluated with regard to its possible application in on-board mobile and portable power sources. In this study, the aluminum–water reaction induced by Co–Fe–B has been examined. SEM results have shown that the chain-like Co–Fe–B catalyst forms a network structure under the influence of an external magnetic field. Co–Fe–B is actually a mixture of cubic Fe and amorphous Co–Fe–B. The Fe content in Co–Fe–B increases with increasing mass of FeCl₃ used in its synthesis. An increase in the Fe content in Co–Fe–B shortens the induction time and improves the amount of hydrogen generated owing to the formation of Fe/Al, Co–Fe–B/Al, and Co–Fe–B/Fe micro galvanic cells. However, an increase in the Co–Fe–B content slightly decreases the amount of hydrogen generated owing to its agglomeration and oxidation. With increasing temperature, both the reaction rate and the amount of hydrogen generated are improved. The activation energy of this reaction, calculated from the maximum reaction rates at different temperatures, is 40 kJ mol⁻¹. Hydrogen is rapidly generated, without an induction time, upon the addition of consecutive batches of Al, because the occurrence of the high concentration of OH⁻ ions effectively accelerates the corrosion of Al.

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Introduction

Hydrogen generation by the corrosion of aluminum in aqueous solution has attracted much attention because this reaction is easy to control and the cost is relatively low. The obtained hydrogen is of high purity and can be used as an energy source in mobile and portable applications. Unfortunately, the aluminum–water reaction is inhibited by the presence of a protective oxide layer. This oxide film is generally removed by treatment with alkaline solution according to Equation (1).



Moreover, decreasing the particle size of Al, increasing the reaction temperature, or a change of medium (alkaline, weak acid, sea water) can all accelerate hydrogen generation [1–3]. Besides these methods, other strategies are used to destroy the oxide film to enhance the corrosion of aluminum and promote hydrogen generation. Mixtures of Al and other metals (Ga, Bi, In) prepared by ball milling display higher reactivity than pure aluminum due to reinforcement of the micro galvanic cell [4,5]. Mixing Al and metal oxides (TiO₂, Co₃O₄) improves the production of hydrogen owing to a pitting

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process originating from point defects [6]. The addition of γ - Al_2O_3 to Al decreases the induction time of the aluminum–water reaction, which is attributed to dissociation of H_2O at the oxide surface [7]. The formation of $\text{Al}(\text{OH})_3$ with the high surface area and the poor crystallinity greatly enhances the aluminum–water reaction [8]. The addition of a metal, metal oxide or $\text{Al}(\text{OH})_3$ as a modifier, however cobalt–iron–boron as the catalyst has not been studied.

Amorphous cobalt–iron–boron (Co–Fe–B) prepared by a reduction method shows high catalytic activity in the hydrolysis of NaBH_4 due to electron transfer from B and Fe to active Co sites, and the dispersion of this catalyst can be improved by the addition of Fe_2O_3 [9,10]. However, no studies concerning the effect of Co–Fe–B on the aluminum–water reaction have been reported. In this work, Co–Fe–B has been obtained as a by-product of NaBH_4 hydrolysis in solutions containing Co^{2+} and Fe^{3+} ions. It could be easily recovered from the spent NaBH_4 solution by virtue of its magnetic property. Its catalytic behavior towards the aluminum–water reaction at 45 °C has been tested. Based on the data obtained, the catalytic effect of Co–Fe–B on the aluminum–water reaction is discussed.

Experimental

Preparation of the catalyst

As raw materials, aluminum powder (Tianjin Damao Chemistry Reagent Factory, China, Tianjin; 99.0% purity), NaBH_4 (99.0%), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (99.0%) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Tianjin Bodi Chemical Co., China) were used in this study.

The Co–Fe–B catalyst was synthesized by the conventional wet-chemical reduction method. Typically, Co–Fe–B was obtained by adding sodium borohydride (0.2 g) to a 20 mL solution containing $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.5 g) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ($x_{\text{FeCl}_3} = 0.1$ –1.0 g) without stirring. A magnetic stirrer bar provided an external magnetic field allowing collection of the particles by virtue of their magnetic property. The black Co–Fe–B precipitate adhered on the surface of magnetic stirrer bar, allowing its easy separation from the mixture. The powder was washed with water to remove remaining Cl^- and Na^+ ions. Finally, it was washed with ethanol and dried at room temperature.

Hydrogen generation measurement

A mixture of Co–Fe–B (0.02 g) and Al (0.2 g) that had been manually blended for 3 min was placed in 30 mL deionized water and sealed in a flask. The flask was sealed immersed in a water bath to maintain constant temperature, and the contents were stirred. After the initial reaction, the 1st batch and the consecutive batches of pristine Al were added to the same flask. The byproduct $\text{Al}(\text{OH})_3$ was accumulated in this reaction. The hydrogen produced was collected in an inverted burette completely filled with water. The volume of hydrogen produced over 400 min was recorded at 10 min intervals from the change in the water level in the inverted burette.

Characterization

The structure of Co–Fe–B was determined on a Bruker D8 Advance X-ray diffractometer (XRD) employing $\text{Cu-K}\alpha$ radiation and operated at a voltage of 40 kV and a current of 40 mA. The morphology of the products was investigated by means of an S-4800 field-emission scanning electron microscope (FE-SEM), equipped with an Energy Dispersive Spectroscopy (EDX) analyzer enabling semiquantitative analysis. In order to examine the specific surface area of the product, Brunauer–Emmett–Teller (BET) surface area measurement was performed at -196 °C on a Quantachrome NOVA 4000 apparatus. Surface electronic states and valence states were studied by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD multi-technique).

Results and discussion

Al and Co–Fe–B

Fig. 1 shows SEM image (a) and the XRD pattern (b) of pristine Al. It can be seen that the particle size of the pristine Al was inhomogeneous, ranging from nano-sized to micro-sized. Some of the particles were enlarged elliptical and some were close to spherical. The surface of these particles was compact and uneven. The XRD pattern showed only the standard peaks of Al (JCPDS card no. 74-1657), suggesting high purity of this pristine sample.

Generally, NaBH_4 reacts rapidly with water to produce hydrogen. NaOH acts as an inhibitor of this hydrolysis of NaBH_4 . In order to avoid the possible presence of OH^- ions in the Co–Fe–B powder, the catalyst was prepared by the hydrolysis of NaBH_4 in a solution containing Co^{2+} ions without the addition of NaOH. The black Co–Fe–B powders accumulated on the surface of the magnetic stirrer bar (inset in Fig. 2), by virtue of its ferromagnetism.

With the masses of NaBH_4 and Co kept fixed, the evolution of the morphology of the prepared Co–Fe–B with increasing mass of FeCl_3 is shown in Fig. 2. When the mass of FeCl_3 was 0.1 g, Co–Fe–B particles with an average size of <100 nm were obtained. When the mass of FeCl_3 was increased, the particles became interconnected and formed chain-like structures under the influence of the external magnetic field. This chain-like Co–Fe–B overlapped and formed a network structure. Concomitantly, the specific surface area calculated from BET data increased from 22.38 ($x_{\text{FeCl}_3} = 0.1$ g) to 54.96 $\text{m}^2 \text{g}^{-1}$ ($x_{\text{FeCl}_3} = 1.0$ g).

The relative Fe/Co composition in Co–Fe–B was determined by EDX analysis, as shown in Table 1. At $\text{Fe}/\text{Fe} + \text{Co} = 17\%$ ($x_{\text{FeCl}_3} = 0.1$ g), amorphous Co–Fe–B was formed, as shown in Fig. 3. The peaks at $2\theta \approx 45^\circ$ and 65° became stronger as x_{FeCl_3} was increased from 0.3 to 1.0 g. These are attributed to the (110) and (200) planes of cubic Fe with space group $Pm\bar{3}m$. The increased intensity of these peaks indicates increased content of reduced metallic Fe. Concomitantly, the ratio $\text{Fe}/\text{Fe} + \text{Co}$ in the Co–Fe–B increased from 35% to 65%, as detected by EDX. The Co–Fe–B catalyst was thus a mixture of Co–Fe–B and metallic Fe.

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