

Research on hydrogen generation from rapid hydrolysis of aluminum in sodium fluoride solution

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Abstract. Hydrogen generation from rapid hydrolysis of aluminum in sodium fluoride solution was investigated through a hydrolysis experiment. Rapid and instant hydrogen yield were observed using sodium fluoride as additive. The experimental results demonstrate that the increase of temperature and the amount of additives in a certain range will boost the hydrogen production. The amount of additives outside the range only has an effect on the rapid hydrolysis of the aluminum during the initial stage, but the total amount of hydrogen produced doesn't increased significantly. Theoretical analysis of the effects of the mixing ratio and the temperature on the hydrogen production rates were performed using the shrinking core model and the kinetic model. The shrinking core model parameter a and k indicate the film change degree of porosity and thickness and the effect of time on the diffusion coefficient. the kinetic model is verified and the activation energy confirming hydrogen yield control by a molecular diffusion process. Correspondingly, mechanisms of Al corrosion in NaF solutions under low and high alkalinity were proposed, respectively.

1 Introduction

As a clean energy source, hydrogen occupies many advantages as high energy density abundant resource, and environment friendly. Fossil energy unable to meet the growing energy demand and release heavy metal pollutant after combustion, causing serious nuisance to the environment[1]. Hydrogen is widely applied in petroleum, metallurgy, chemical industry, fuel cell, aerospace and other fields. With the huge and continuous expenditure of traditional fossil fuel hydrogen produce equipment, a great deal of energy is wasted in the process of producing hydrogen, the requirement of sustainable will not be met at the same time[2].

The reaction of active metals including Na, Mg, Al and Zn with water and alkaline solution to produce hydrogen has been widely studied[2-5]. Among these metals, Al has the highest hydrogen production per unit mass and volume hydrogen production, the lowest cost and the most abundant reserves. On the other hand, the major product of the Al/H₂O reaction is Al₂O₃, which has no pollution to the environment. Furthermore, the recycle technology of Al₂O₃ as industries material are relatively mature.

A dense oxide film is formed on the Al particle surface when exposed in the air, which inhibits its reaction with water[6]. Consequently, how to remove the oxide film becomes a vital factor impacting the hydrogen production rate. After packaging, the thickness of nano-aluminum shell becomes stable, usually maintained at about 3nm. When the nano-aluminum particles is added to the water with higher temperature, the oxide film on

the surface will hydrolyzed and hydrogen generated. As the reaction progresses, an aluminum oxide film is formed to cover the surface of the aluminum particles to inhibit the reaction.

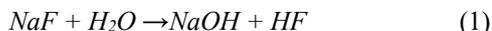
Nowadays, the commonly used methods for removing the film and increasing the hydrogen yield rate are as follows: additives, such as the alkaline salts or other water-soluble inorganic salts, can cause local pitting on the surface of the membrane[7, 8]; mechanical cutting, such as ball milling with metal or metal salts with higher active aluminum content than aluminium, causes fracture on the oxide film on the surface of aluminium, and forming a potential difference between the water and the highly active metal to accelerate the removal of the oxide film; enhancing the reaction temperature and accelerating molecular diffusion to accelerate the density change of the film. Although these methods have proven effective, the treatment process is too complicated, and the use of additives can eliminate the cumbersome steps.

Hydrogen production from an alkaline solution is a widely applied method at present. The activation of OH⁻ in an alkaline solution boosts the hydrolysis process of the surface alumina layer.

Alkaline solution has been considered as one of the most economically proficient catalysts for aluminum reaction[9]. Hence, reaction of aluminum with alkaline solutions can generate considerable amount of hydrogen[10].

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NaF is relatively cheap in manufacturing cost, as well as less deliquescent compared with NaOH. In addition, the rapid development of NaF in a wide range of applications. Demand in industries such as metal smelting, metal surface treatment, ceramics and glass manufacturing has grown significantly. Furthermore, the increase in temperature has little effect on the solubility. NaF is used in our experiments to meet different directions of research requirements[11]. The reactions of NaF solution with aluminum are presented as follows:



In the current work, hydrogen generation from rapid hydrolysis of aluminum in sodium fluoride solution was investigated through a hydrolysis experiment. Theoretical analysis of the effects of the mixing ratio and the temperature on the hydrogen production rates were performed using the shrinking core model and the kinetic model. Mechanisms of Al corrosion in NaF solutions under low and high alkalinity were proposed, respectively.

2 Experimental details

The experiment selected spherical aluminum particles produced by electric explosion method with particles size of 80 nm and purity of 99.9% produced by Mao Gon Nanometer Material Limited Company in Shanghai. The metallic aluminum content of the Al nanopowders was about 94.1% which was measured by gas volumetric method. The sodium fluoride was manufactured by Shanghai Sinopharm Group. The hydrogen production apparatus used in the experiment adopted the traditional drainage method, and the hydrogen was collected and measured by the cylinder. NaF (0.125–0.75 g) and nano aluminum particles (0.15g) were firstly added to 30mL deionized water (pH = 6.7) in 150mL flask at 50°C. This mixture was stirred using a magnetic stirrer which rotating speed was kept constantly to accelerate the reaction of NaF with water to obtain the low concentration alkali solution. Each experiments was repeated more than three times to got the parallel record. Under standard conditions, 1.0 g aluminum particles can produced 0.272 L H₂ in theoretical. The schematic diagram of the experimental device was presented in fig.1.

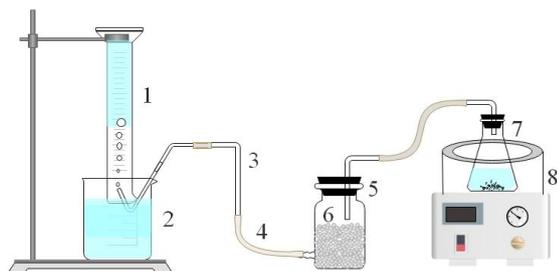


Fig. 1. Experimental setup for measuring the hydrogen yield.

1. Measuring cylinder; 2. Water container; 3. Glass tube; 4. Silicon rubber tube; 5. Tubulated bottle; 6. Desiccant; 7. Pyrex conical flask reactor; 8. Magnetic stirrer apparatus.

3 Theoretical models

In order to get a deeper insight into kinetics of the H₂ generation process from Al particles in low and high alkaline solution, obtained results for experiments carried out with NaF additive are analyzed using two different models[12]. S.S. Razavi-Tousi et al. discovered that the traditional shrinking model the overall size of the particle is unchanged during the reaction, however, in shrinking core model the size of the particle increases and the radius of the particle changes from R_0 to R [13]. For the sake of understand heterogeneous kinetics of hydrogen generation process, Arrhenius equation for solid–liquid systems are tested. Soler. L et al. founded this kinetics model usually depend on the degree of reaction k , The obtained results are analyzed using two different approach. One controlled by reaction kinetics and one controlled by diffusion of water molecules in the generated layer[14]. The reaction rate and by-product intensively depend on pH and temperature of solution. The hydroxide species formed as by-product is soluble in solutions with pH higher than 11[13]. Therefore, the shrinking core model is suitable when the pH was lower than 11.

3.1 Shrinking core model

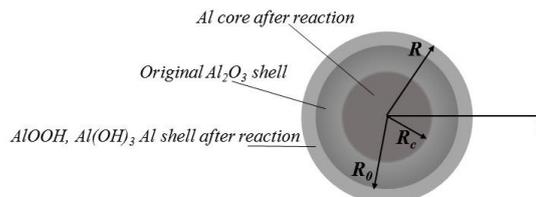


Fig. 2. The schematic of the modified shrinking model.

The shrinking core model is based on the equation proposed by S.S. Razavi-Tousi[13]. The schematic of the model is presented in fig. 2. R_0 is the original particle size, and R is the particle size after the reaction. The model assumes that the particle size increases from R_0 to R during the reaction, and the thickness of the shell film and the thickness of the consumed aluminum core are constantly changing during the reaction[13]. The process can be written as:

$$V_R = V_{Rc} + V_x \quad (3)$$

V_R is the volume of the aluminum particle after the reaction, V_{Rc} is the volume of the remaining aluminum core after the reaction, and V_x is the volume of the film formed by the aluminum nuclear reaction. It is defined that n is the ratio of the volume of the aluminum nuclear reaction-forming membrane to the volume of the

consumed aluminum core. Then the above equation can be written as:

$$V_x = n(V_{R0} - V_{Rc}) \quad (4)$$

Defining X_b for the conversion of nuclear aluminum to hydroxides can be described as:

$$X_b = 1 - \left(\frac{R_c}{R_0} \right) \quad (5)$$

The model reaction equation established by S.S. Razavi-Tousi is composed as:

$$n + (1-n)(1-X_b)^{\frac{2}{3}} - [n + (1-n)(1-X_b)]^{\frac{2}{3}} = -\frac{2bD_0C_{A0}(1-n)}{k\rho R_0^2} \ln(kt+1) \quad (6)$$

The parameter b is taken the value 0.5. Due to the porous structure of the shell membrane, D_0 is the diffusion coefficient of water molecules penetrating the shell membrane. The pore density and water molecule permeability of the shell film vary from time during the reaction, and k determines the effect of time on the diffusion coefficient[13]. The molar amount of aluminum particles per unit volume is 0.1mol/cm^3 , the density of Al is 2.7g/cm^3 , the density of AlOOH is 3.03g/cm^3 . The molar volumes are 27g/mol and 60g/mol , respectively, so that the volume of the resulting membrane is about twice the volume which aluminum consumed, so n can be taken the value 2.

When each parameter take different value, it will have a greater impact on the fitting result in equation (6). So it will be converted equation (7) to make the fitting easier, except that D_0 and k are unknown. In addition to known parameters to be fitted, value of unknown parameters are substituted, the equation (7) is integrated into the parameter a , a express the change degree of film density and porosity. t is transformed into a function with X_b as the independent variable, and the original equation is transformed into the following equation (8).

$$a = -\frac{2bD_0C_{A0}(1-n)}{k\rho R_0^2} \quad (7)$$

$$t = \frac{e^{\left\{ a \left[2 - (1-x)^{\frac{2}{3}} - [2 - (1-x)^{\frac{2}{3}}] \right] \right\}} - 1}{k} \quad (8)$$

3.2 Heterogeneous kinetic model

When the pH value is higher than 11, the shrinking core model is not applicable since the alumina shell formed during the process quickly dissolves in the alkaline solution, the aluminum/water reaction is mostly controlled by the reaction kinetic. In order to comprehend the kinetic of the hydrogen generation procedure, kinetic model be used to obtain k_{ex} at different temperatures, and can calculate apparent activation energy by k_{ex} . Apparent activation energy is mainly used to explain the effect of temperature on hydrogen production. Equation (9) can be applied to

describe the kinetic controlled process. α represents the degree of reaction, which is the ratio “reacted quality /initial quality”[14]. k_{ex} is the apparent reaction constant.

$$\frac{1 - (1 - \alpha)^{\frac{1}{3}}}{t} = k_{ex} \quad (9)$$

4 Results and discussion

4.1 Effect of temperature on hydrogen production

When the temperature was lower than 50°C , almost no hydrogen was generated from the aluminum water reaction, and the essentially impractical induction times was too long at low temperature[15]. When the temperature exceeded 50°C , the reaction rate was significantly accelerated[16]. Hydrogen yield curves at each temperature were shown in fig. 3. At 60°C , 70°C and 80°C , the corresponding hydrogen yields were 68.60%, 82.35% and 88.73%, respectively. Since the 80nm aluminum particles had higher activity, the hydrogen yield was closed to 89% at 80°C .

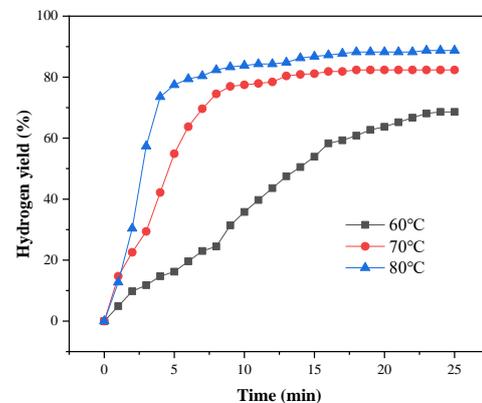


Fig. 3. Hydrogen generation curves at different temperature for Al/H₂O reaction

It can be seen from the fig. 3 that the slope of the curve certificated that the reaction rate increased significantly with the promoted of temperature, as well as the hydrogen yield was enhanced. Besides, the hydrolysis process on the surface oxide film was accelerated, the aluminum water reaction was an exothermic process, which improved hydrogen production performance and advanced progress of various chemical reactions.

4.2 Effect of sodium fluoride addition on hydrogen production

By compared the temperature of the aluminum water reaction, 70°C and 80°C were selected as the experimental temperature. At 70°C , The hydrogen yield and produce hydrogen flow rate curve at 70°C was revealed in fig. 4 and fig. 5.

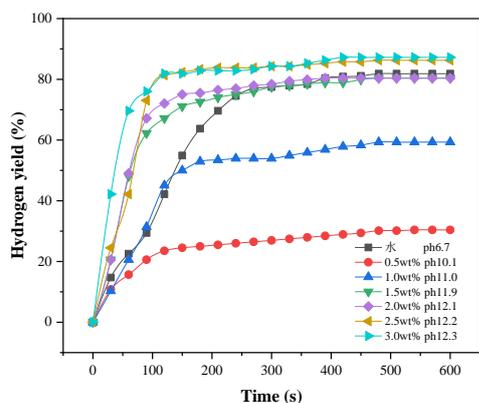


Fig. 4. Hydrogen yield of the Al/H₂O reaction with different NaF concentrations at 70°C.

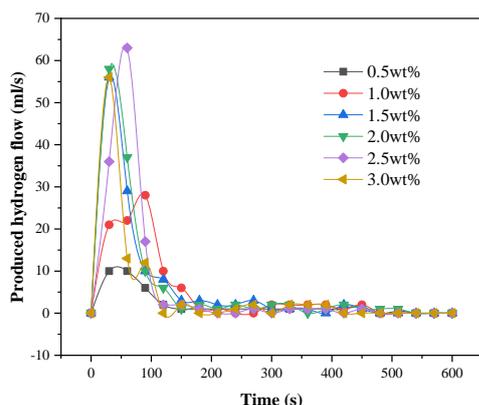


Fig. 5. Produced hydrogen flow rate vs. time for experiments conducted with aluminum particles at 70°C.

Hydrogen yield in reaction was affected by various factors, such as the pH value, temperature, rotor speed, etc[4, 5]. The temperature and other setting conditions were kept constant during the experiment in order to studied the effect of different amount of additives on the hydrogen filed at 70°C. It can be seen that the amount of the hydrogen was evidently increased when the amount of the supplement from 0.5wt% to 1.0wt% and 1.5wt%. When the mass concentration of NaF was less than 1.5% , F⁻ and Na⁺ dissolved in water were totally ionized, but only a few F⁻ was hydrolyzed[17, 18]. Although the solution was alkaline, the concentration of F⁻ in water was larger than OH⁻ in low alkalinity. Surprisingly, Hydrogen yield was less than the reaction with water when in 0.5wt% and 1.0wt%. The time of the induction phase was shortened when the mass concentration of sodium fluoride above 1.5 wt%. NaF was hydrolyzed to form NaOH and a small amount of HF, which increases the concentration of OH⁻ in the water, which accelerated the hydrolysis process and enhanced hydrogen yield. When the amount of the additive was increased to 2.5wt%, the hydrogen yield reached maximum value about 87%. With the increased of additive to 3.0wt%, the time required for hydrogen generation was shortened, but the maximum hydrogen flow and hydrogen yield were almost no longer improved.

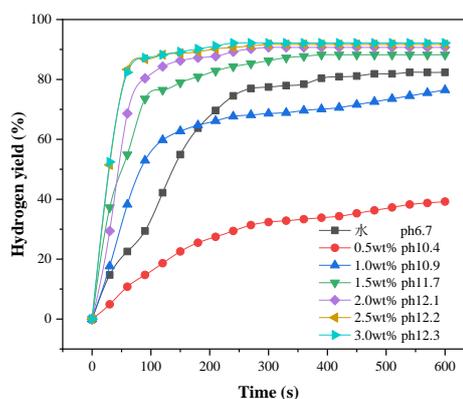


Fig. 6. Curves of hydrogen evolution of Al/H₂O reaction with different NaF concentration at 80°C

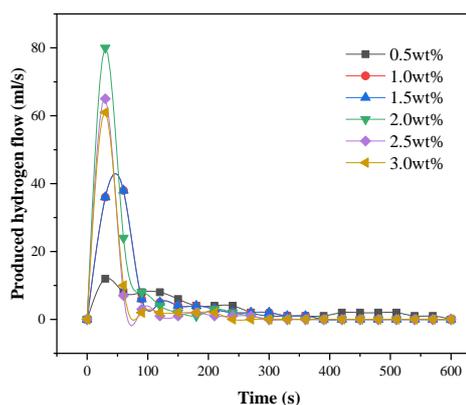


Fig. 7. Produced hydrogen flow rate vs. time for experiments conducted with aluminum particles at 80°C.

At 80°C, The hydrogen production yield and hydrogen production flow curves at 80°C was shown in fig. 6 and fig. 7. The higher temperature promoted the hydrolysis of the membrane, accelerated the rate of ion permeation through the membrane[8, 9, 19]. When the amount of the additive was 2.5wt%, the hydrogen yield was not apparently changed as compared with 2.0wt%, so that the hydrogen yield reached the most desirable result when the amount of NaF added in 2.0wt%. The promotion of temperature reduced the requirement of NaF for the maximum gas flow rate and the maximum hydrogen yield. In the first minute of the reaction, the hydrogen production rate could reached nearly 80% in the 2.0wt% or above this quantity, the gas flow rate peaked at the same time within 1 min.

4.3 Theoretical analysis of the effects of NaF addition on Al/H₂O reaction

The volume change of Al powder during the reaction is mainly caused by the shell membrane and the core contraction, the degree of reaction mainly depends on the pH and temperature. The shrinking core model is assumed that both the particle size and the porosity of the membrane are changed during the reaction. The formed hydroxide by the reaction is soluble in the pH range of 2-11 following the diffusion of ions and water molecules[13]. When the solution temperature is at 70°C,

the pH value is 0.5wt% and 1.0wt% in this range. In the shrinking core model, only the data at 0.5wt% and 1.0wt% were discussed. When pH not within this range, so the corresponding kinetic model is established. The discuss of hydrogen production kinetic can indicates the relationship between activation energy and suitable mixing ratio. Based on the experimental data, the kinetic model can be used to studies the experimental data of 1.5wt% and above. In order to further understand the hydrogen production rate of aluminum particles in an alkaline solution at different temperature, an appropriate amount of NaF is selected to be 2.0wt% and 2.5wt% applied to the kinetic model.

4.3.1. Mechanism under low alkalinity

The shrinking core model was applied to analyze the experimental data obtained with 0.5wt% and 1.0wt% NaF solutions. According to the fitting curves obtained by experiments, the initial induction phase and the rapid reaction phase could be converted into one stage, the entire reaction was divided into two stages before and after the dotted line in the fig. 8. In the first half of the stage, due to the influence of additive and temperature, the surface film hydrated rapidly. Density of the film decreased and pores became larger, as well as the aluminum core reacts to formed new shell membrane. Therefore, the hydroxide layer formed in the initial stage of the reaction has a higher water permeability and reaction rate[20-22]. As the reaction proceeded in second stage, the thickness of the shell film increased, and it is founded that the thickness of the shell film produced was not uniform, the particle size was also increased before the reaction. The water permeability decreased at the same time. The reaction became slow down accordingly. The transform of shell film thickness and density were major factors affecting the water permeability reaction. It can be seen from the fig. 2 that when X_b was close to 0.5, the rate of conversion of aluminum nuclear to hydroxide was significantly accelerated, and the middle part of the thickness of the entire aluminum core was consumed. The result of the fitting was presented in fig. 8.

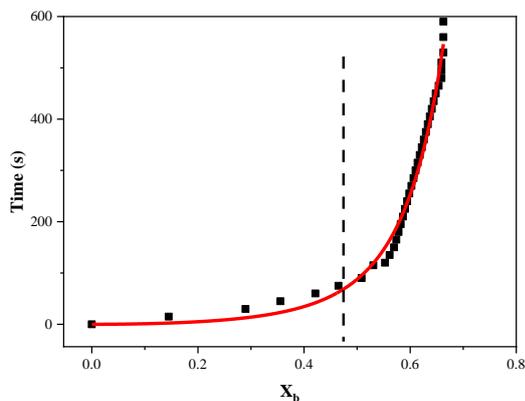


Fig. 8. Fitting the data obtained from reaction of Al/0.5wt%NaF at 70°C with the modified shrinking core model.

the k describe diffusion coefficient changed over time. a represent the film change degree of porosity and thickness. The hydroxide layer changes from thin and porous in the initial stage to thick and dense, and supplements result in Al micro-structure variety. When the NaF additive increased from 0.5wt% to 1.0wt%, Parameters k and a both increased. The advance in the mass fraction of sodium fluoride will augment the extent of diffusion within the applicable pH range as shown in table 1.

Table 1. Parameters obtained from fitting the modified model to the experimental data from hydrogen production.

NaF	a	k	R^2
0.5wt%	32.87	0.068	0.986
1.0wt%	34.26	0.085	0.991

4.3.2. Mechanism under high alkalinity

When the pH value was higher than 11, the kinetic model was selected to analyzed the experimental data. It can be observed from fig 9 and 10 that higher hydrogen yield can be achieved by using 2.0wt% and 2.5wt% at low temperature. For example, Linear fitting of the hydrogen yield at 2.5wt% NaF in initial rapid reaction stage. By linear fitting, k_{ex} can be obtained under the 2.5wt% NaF. The activation energy was obtained through fitting experimental data presented in fig. 12 and fig. 13.

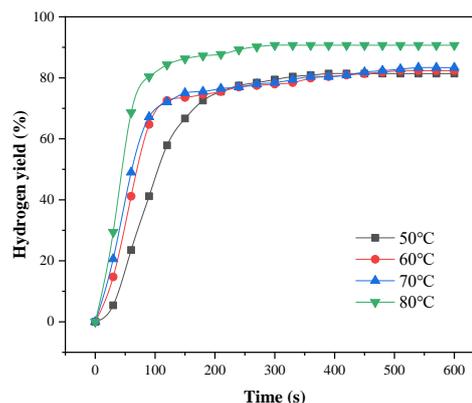


Fig. 9. The hydrogen yields of Al/2.0wt% NaF at different temperatures.

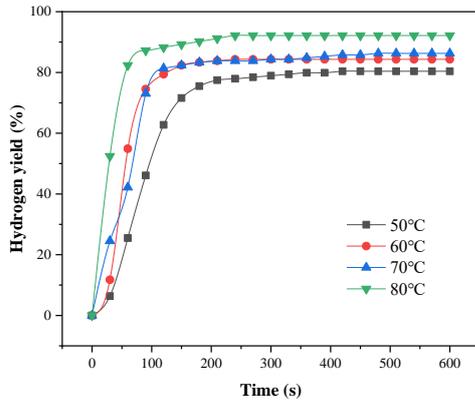


Fig. 10. The hydrogen yields of Al/2.5wt% NaF at different temperatures.

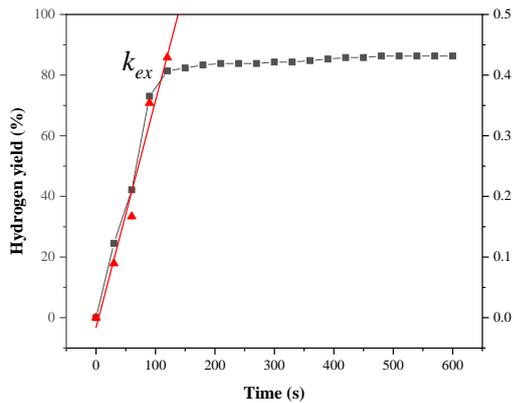


Fig. 11. Fitting of the experimental data obtained using 2.5wt% NaF solution at 70°C using the kinetic model .

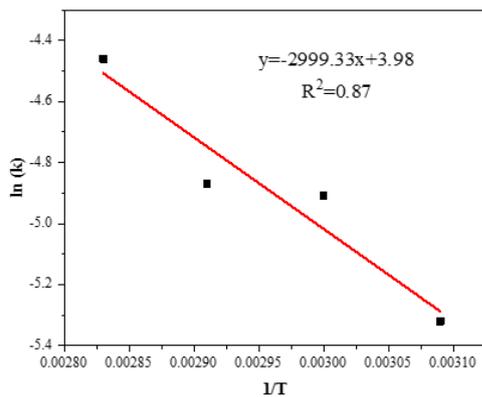


Fig. 12. Arrhenius plot of the rate constants using 2.0wt%NaF solution.

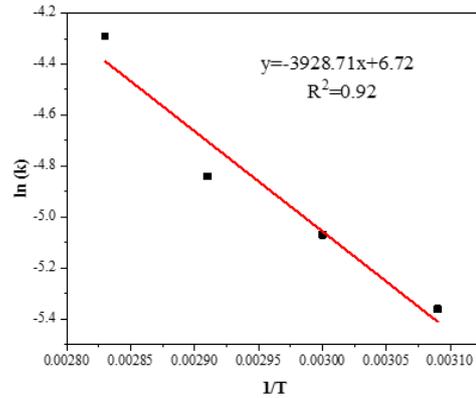


Fig. 13. Arrhenius plot of the rate constants using 2.5wt%NaF solution.

The Arrhenius equation can be transformed into the following expression.

$$\ln k_{ex} = -\frac{E_a}{RT} + \ln A \quad (10)$$

The apparent reaction rate constant k_{ex} obtained from dates in 50°C to 80°C was fitted using the hydrogen yield curves from different temperature according to equation (10). The apparent activation energy of reaction obtained from fitted curves were presented in fig. 12 and fig. 13. The relationship between the logarithm of the reaction rate constant k_{ex} and the reciprocal of the temperature, the activation energy of aluminum was 24.9kJ/mol at 2.0wt%, and the activation energy of aluminum at 2.5wt% was 29.3kJ/mol. The lower activation energy indicated that the reaction was easier to carry out, which meant that the membrane undergoing faster hydrolysis and causing quick hydrogen generation.

5 Conclusions

In this work, the effect of mass concentration of NaF additive and temperature were researched on hydrogen yield from Al. By means of experimental data, the shrinking core model and kinetic model were proposed for low and high alkalinity respectively. Through the analysis of date, we get following conclusions:

1. The hydrogen yield reached the optimum value at 70°C, 2.0wt%. At 2.0wt% and 2.5wt%, when using a lower temperature, the hydrogen yield can reach 80% or more. As the amount of additive increases to more than 2.5wt%, the maximum hydrogen yield does not change significantly, and only affects the rapid hydrolysis of the shell film during the accelerated induction phase.
2. When the pH value is lower than 11, only 0.5wt% and 1.0wt% of the experimental data were applied to the shrinking core model. Parameters k and a both increase when the NaF mass concentration increases from 0.5wt% to 1.0wt%. Promotion of parameters a and k lead to expanded porosity and reduced the density of membrane, advancing water molecule permeability.
3. When the pH value is higher than 11, through applying the kinetic model, the activation energy of the addition amount of NaF at 2.0wt% and 2.5wt% is

calculated and compared. the activation energy of aluminum was 24.9kJ/mol at 2.0wt% and 2.5wt% was 29.3kJ/mol. Activation energy are close and low at 2.0wt% and 2.5wt%, Lower activation energy also make the reaction easier to occur.

Acknowledgments

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