Hydrogen production by aluminum corrosion: Experimental investigation and mathematical modeling

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Abstract. The search for new energy sources has been a great focus lately because of concerns about climate change caused mainly by fossil fuels gas emissions. The hydrogen is a promising energy source due its clean and high energy combustion. However, the major drawbacks to use hydrogen are the difficulty of formation, transportation and storage. The objective of this work is the study of hydrogen formation by aluminium reaction with water by using strong alkalis as catalysts (NaOH and KOH), and the development of a mathematical model that accounts the evolution of hydrogen at each time. Different alkali concentrations were used (1, 1.5, 2, 2.5 and 3 mol·L^{-1}). The reactions were carried out with aluminum in different samples: foils, plates with 0.5 mm and 1 mm width each. The range of temperatures studied was: 295, 305, 315 and 325 K for foils and 0.5 mm plates; 315, 325, 335 and 345 K for 1 mm plates. The results showed a strong dependence of the reaction rate on the temperature, alkali concentration and shape of the samples. The model predictions of hydrogen formation agreed with the experimental data of volume *versus* time, as well as the peaks observed in the reaction rates.

Key words

hydrogen, fuel cell, aluminum, alkaline corrosion

1. Introduction

Several investigations about new energy sources have been carried out during the last decades. Concerns about a possible depletion of petroleum, coal and gas, as well as new methods to achieve a more reasonable use of these raw materials to obtain energy have been widely investigated at present, especially some studies about the reduction of green house gases.

The hydrogen has a very high combustion heat (HHV = 141.90 kJ·g^{-1}, LHV = 119.9 kJ·g^{-1}), which is a promising alternative in terms of energy. However, hydrogen must be generated by means of some chemical reaction, because this gas is not encountered available as "H_2" in nature. It is also a very difficult liquefying H_2 to be transported or stored ([1]). Based upon these considerations, the objective of this work is the production of high purity hydrogen via aluminum-water reaction by applying a catalyst to speed up the rate of gas formation. The presence of the catalyst (strong alkali, NaOH and KOH) is necessary because the reaction of the metal with water does not occur due to presence of a very thin passivation layer, Al_2O_3, which hinders the reaction ([6] e [3]). The use of alkalis, like NaOH and KOH, promotes the complete removal of this layer, so that the reaction with water may proceed ([4], [5]). The reaction that occurs is as follow:

$$Al + 3H_2O \rightarrow Al(OH)_3 + \frac{3}{2}H_2$$

Different mechanisms have been proposed for the reaction presented. In [8], the formation of an intermediate (pseudoboehmite, AlOOH) was considered in a mathematical approach that accounts for the pressure of the hydrogen bubbles formed under the metal surface, thickness of the hydrated oxide film, and other effects. Also, $NaAl(OH)_4$ was considered an intermediate compound, and the replacement of NaOH by $NaAlO_2$ as catalyst was successfully verified ([4],[5]).

2. Experimental apparatus

The reactions were performed in an inverted and sealed 60 mL syringe where, both alkali solutions and aluminum samples (range about 34-37 mg of metal) were inserted. The syringes were immersed in a thermostatic water bath up to the level of alkali solution (5 mL), as depicted in Figure 1.

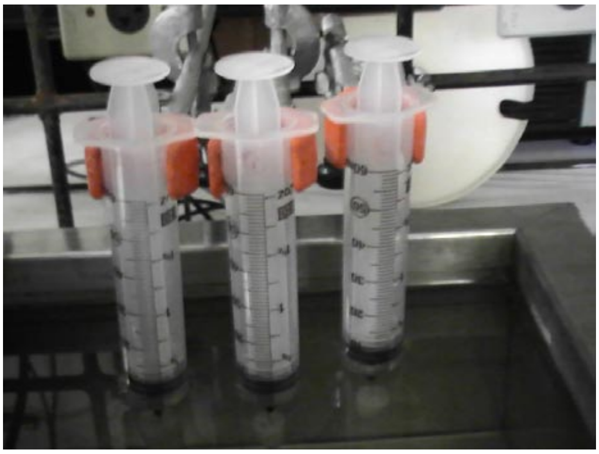

Figure 1 - Illustration of the experimental apparatus.

The needles were inserted in silicone stopper to avoid leaking of solution inside the thermostatic water bath. Hydrogen formation was measured by displacement of the piston during time and registering the corresponding volume of gas. Three experiments were done for each concentration of alkali at each temperature. A correction factor ($T_{\text{water bath}}$ / $T_{\text{room temperature}}$) was used because the temperature of hydrogen formation in the lower region of the syringe immersed in the bath was different of that in the remaining syringe due to the influence of room temperature. Thus, the number of moles calculated must take into account this difference.

3. Mathematical modeling

The model proposed has the objective of capturing the full behaviour of the entire curve of hydrogen formation. Models that describe the reaction controlled steps are very common in literature ([2]), but normally the mass transfer step at the end of the process is neglected or does not fit to the curves. The equation (1) expresses the reaction rate as a zero-order reaction and as a function of the Sherwood number, S*h*:

$$r_{H_2} = kC_{alkali}Sh \tag{1}$$

In equation (1), r_{H2} is the hydrogen formation rate, expressed in $\text{mol}\cdot\text{cm}^{-3}\cdot\text{min}^{-1}$, k is the kinetic parameter expressed as min^{-1} and C_{alkali} is the molar concentration of NaOH or KOH, $\text{mol}\cdot\text{cm}^{-3}$. The Sherwood number is:

$$Sh = \frac{k_c\delta}{D_{H_2}} \tag{2}$$

The term k_c is the mass transfer coefficient, in $\text{cm}\cdot\text{min}^{-1}$, δ is a dimensional parameter that represents a length factor of the metal samples (hydraulic length) where the bubbles move along in the extent of the reaction, expressed in cm, and D_{H2} is the diffusivity of hydrogen gas, expressed as $\text{cm}^{2}\cdot\text{min}^{-1}$. The reaction rate is directly based upon the hydrogen production instead of aluminum consumption, because makes the mathematical comparison with experimental data more easy

$$r_{H_2} = \frac{1}{V}\frac{dN_{H_2}}{dt} \tag{3}$$

The number of moles of hydrogen produced may be expressed in the following way:

$$N_{H_2} = N_{H_2}{}^{0} + N_{H_2,prod} \tag{4}$$

where N_{H2} is the number of moles of hydrogen in any time t, $N_{H2}{}^{0}$ is the initial number of moles of hydrogen (zero for this system) and $N_{H2,prod}$ is the number of moles of hydrogen produced, and V is the syringe volume, in cm^3 or mL. This last may be written, according to the stoichiometry of the aluminum-water reaction, as:

$$N_{H_{2},prod} = 1.5N_{Al,cons} = 1.5N_{Al}{}^{0}x \tag{5}$$

The consumed aluminum is expressed based on its initial number of moles times the conversion. By replacing equation (5) in (4), and after in 3, one obtains:

$$r_{H_2} = \frac{1.5N_{Al}{}^{0}}{V_0(1+\varepsilon x)}\frac{dx}{dt} \tag{6}$$

The term $V_0(1+\varepsilon x)$ accounts the expansion of the system during the occurrence of a variable volume reaction cm^3, (as experiment in Figure 1), and ε is the expansion term [7]:

$$\varepsilon = \frac{V(x=1)-V(x=0)}{V(x=0)} \tag{7}$$

The dimensional parameter of the Sherwood number, δ, is expressed as a function of time by a classical linear momentum equation:

$$\delta = \delta(t) = \delta_0 + v_0 t + \frac{at^2}{2} \tag{8}$$

where δ_0, v_0 and a are interpreted as position, velocity and acceleration terms of the gas bubbles formed on the aluminum surface, respectively in cm, $\text{cm}\cdot\text{min}^{-1}$ and $\text{cm}\cdot\text{min}^{-2}$. When one replaces equation (8) in equation (2) and the remaining equation is inserted in equation (1), one obtains:

$$r_{H_2} = kC_{alkali}\frac{k_c}{D_{H_2}}\left(\delta_0 + v_0 t + \frac{at^2}{2}\right) \tag{9}$$

Now, by equalling equations (6) and (9):

$$\frac{1.5N_{Al}{}^{0}}{V_0(1+\varepsilon x)}\frac{dx}{dt} = kC_{alkali}\frac{k_c}{D_{H_2}}\left(\delta_0 + v_0 t + \frac{at^2}{2}\right) \tag{10}$$

After separating the variables x and t in equation (10), the differential equation may be integrated accordingly (from x=0 to x and from t=0 to t), by obtaining the following solution:

$$\ln(1+\varepsilon x) = \left(\frac{\varepsilon k_c k C_{alkali} V_0}{1.5N_{Al}{}^{0}D_{H_2}}\right)\left(\delta_0 t + \frac{v_0 t^2}{2} + \frac{at^3}{6}\right) \tag{11}$$

The term $(1+\varepsilon x)$ is the relation between V and V_0, which takes to:

$$V = V_0 e^{k_{\exp}\left(\delta_0 t + \frac{v_0 t^2}{2} + \frac{at^3}{6}\right)} \tag{12}$$

Being that k_{exp} is a combination of several parameters:

$$k_{\exp} = \left(\frac{\varepsilon k_c k C_{alkali} V_0}{1.5N_{Al}{}^{0}D_{H_2}}\right) \tag{13}$$

The volumetric reaction rate in $cm^3 \cdot min^{-1}$ is calculated by taking the derivative of the equation (12):

$$\frac{dV}{dt} = V_0 k_{\exp} e^{k_{\exp}\left(\delta_0 t + \frac{v_0 t^2}{2} + \frac{a t^3}{6}\right)} \left(\delta_0 + v_0 t + \frac{a t^2}{2}\right) \qquad (14)$$

The parameters in equation (12) were estimated in Matlab, with the use of the tool "LSQCURVEFIT", a nonlinear least-square minimization algorithm.

4. Results and Discussion

Some of the main results are illustrated in figures 2, 3 and 4, concerning aluminum foil.

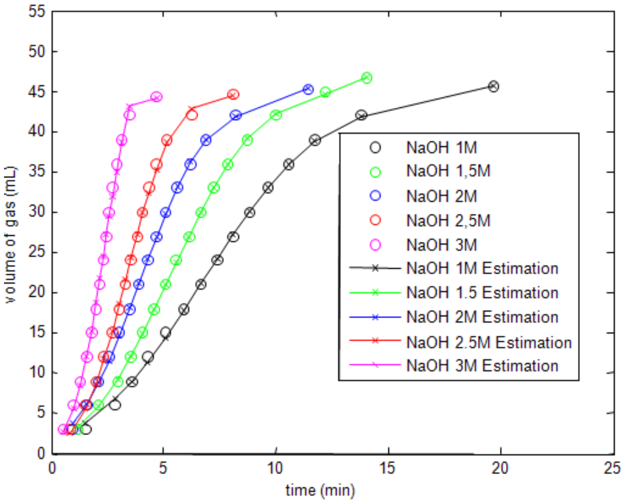

Fig. 2. Production of hydrogen at 295 K - aluminum foil - NaOH - Comparison with equation (12)

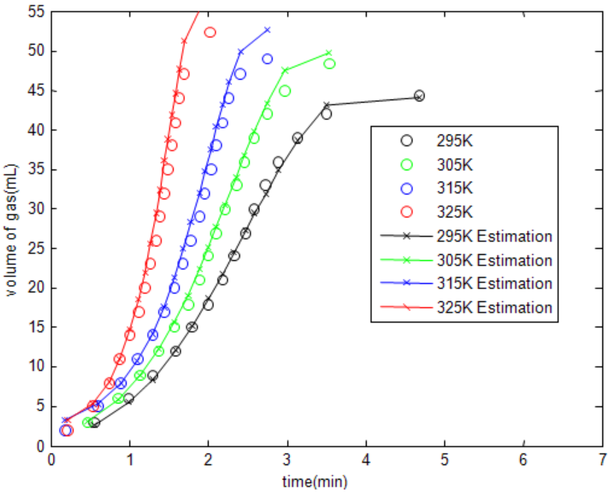

Fig. 3. Production of hydrogen at different temperatures for - NaOH 3M - aluminum foil - Comparison with equation (12)

As depicted in figs. 2 and 3, it is possible observe that the volume of hydrogen evolved is larger the largest is the concentration of the catalyst and the temperature of the medium. This tendency is clearly shown when one plots the experimental reaction rates *versus* the theoretical model described by equation (14), as shown in figure 4.

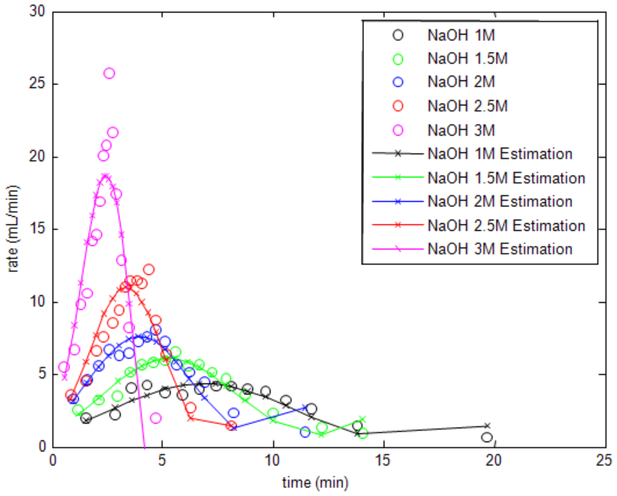

Fig. 4. Reaction rates at 295 K - aluminum foil - NaOH - Comparison with equation (14)

From the results presented in figure 4, it is possible to verify that the model may predict the value and evolution of the peaks relatively to maximum reaction rates. As expected by the theory, the higher is the concentration of the catalyst, the higher is the speed of aluminum consumption. The behavior of the reaction rates with temperature is illustrated in figure 5:

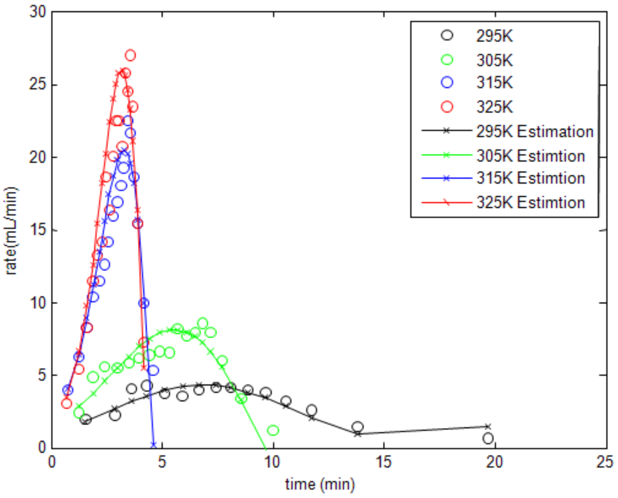

Fig. 5. Reaction rates for aluminum foil - NaOH 1M - Comparison with equation (14)

The curves in figure 5 confirm what is expected by the theory, where the reaction rates are larger the largest is the temperature of operation. It is also possible to verify (in figs 4 and 5) that the intensity of the peaks is displaced for larger times the lower is the temperature and concentration of the alkali. Good predictions of the model were also achieved with KOH as, illustered in figures 6 and 7:

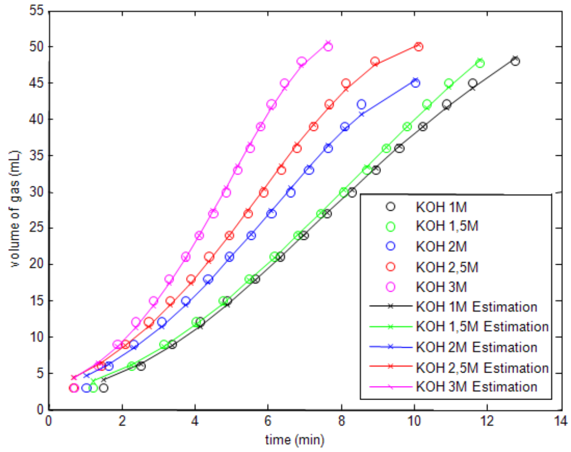

Fig. 6 - Production of hydrogen at 295 K - aluminum foil KOH - Comparison with equation (12)

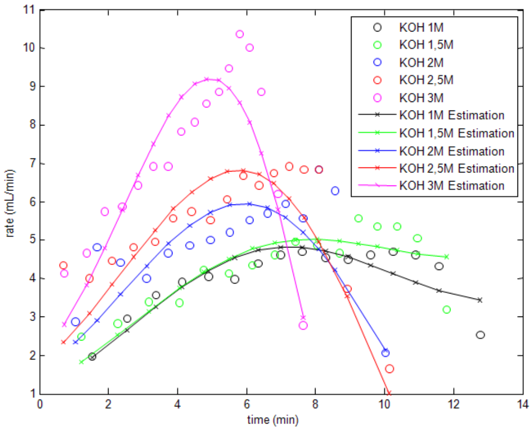

Fig. 4. Rates of reaction at 295 K - aluminum foil - KOH Comparison with equation (14)

By comparison of the curves of KOH with the curves obtained with NaOH, one verifies that the shape of the peaks in the reaction rates is smoother for KOH rather than NaOH. Also, the values of maximum reaction rates are lesser for KOH. The comparison of hydrogen evolution along the time for both alkalis are illustered in figures 6-8 for different metal samples. Only experimental data are shown for a better visualization of the data, without comparison with the model previously developed.

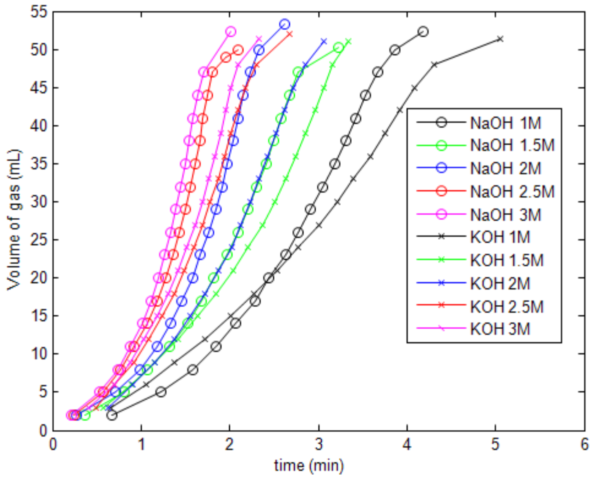

Fig.6. Evolution of hydrogen from aluminum foils for different catalysts concentration - 325 K

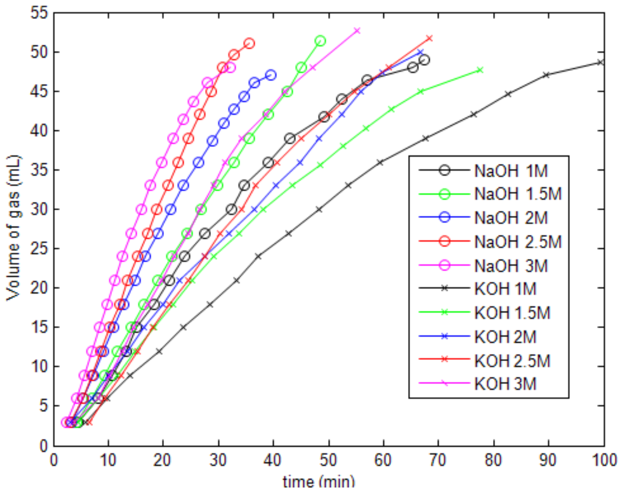

Fig.7. Evolution of hydrogen formation from aluminum plates (0.5 mm width) for different catalysts concentration - 325K

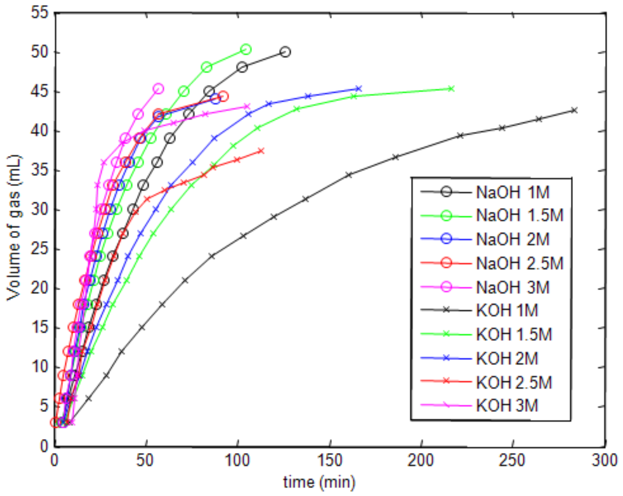

Fig.8. Evolution of hydrogen from aluminum plates (1 mm width) for different catalysts concentration - 325K

The previous results demonstrate that the total time of reaction increases markedly with the metal width, being independent of its mass. This may be explained by the fact that the alkaline corrosion is predominantly a surface reaction, and the reduction of the avalaible metal surface brings as consequence lower values of reaction rates, so increasing the total time.

5. Conclusion

From the previous results presented in this work it is possible to conclude that the aluminum corrosion is strongly influenced by temperature and catalyst concentration. Also, the mathematical model proposed fits the experimental data of hydrogen volume and reaction rate accordingly. Moreover, the speed of aluminum consumption is faster at higher concentrations of alkali, especially when one employs NaOH. KOH presents lower reaction rates for all the samples tested, and these rates decrease sharply the lower is the temperature. Based on these conclusions, this route to obtain high purity hydrogen is a very promising alternative, mainly if recyclable aluminum is to be used as raw material. There is the possibility to apply this system to feed a fuel cell or in connection with other power generation supplies.

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