# Identification of Hydrogen Generation Characteristics from Activated Aluminum Particles Using ARMA Model on the Assumption of the Applications for Fuel-cell Electric Vehicle

**Kenji Takahara [1], Kouji Maekawa [2], Toshinori Kajiwara [3], and Masao Watanabe [4]**

[1] *Department of Electrical Engineering, Fukuoka Institute of Technology, takahara@fit.ac.jp*
[2] *Department of Electrical Engineering, Fukuoka Institute of Technology, mem07012@bene.fit.ac.jp*
[3] *Department of Electrical Engineering, Fukuoka Institute of Technology, kajiwara@ee.fit.ac.jp*
[4] *Hydro-device Co.,Ltd., info@hydro-device.com*

## Abstract

*The purpose of this study is to describe the experiments of hydrogen generation from water molecules reacting with activated aluminum particles and the identification of its characteristics using an ARMA model on the assumption of the applications for a fuel-cell vehicle. Because 1 gram of the activated aluminum particles can generate about 1.1 liters of pure hydrogen, they have application possibility as the hydrogen resource of a fuel cell car. However, the details of hydrogen generation characteristics by this reaction are not well known. The reaction has non-linearity and time-varying due to the characteristics of the sample, the external environment and so on. Therefore, it is difficult to construct a mathematical model based on the physiochemical law of the reaction. Here, the dynamic characteristics of hydrogen generation are assumed to be described as a linear ARMA model using the reaction temperature and hydrogen generation. The parameters of ARMA model are identified by a constant trace adaptive algorithm using the measured data. The outputs of the ARMA model are well accorded with the measured data.*

## Keywords

*hydrogen generation, activated aluminum particles, ARMA model, adaptive identification, fuel-cell electric vehicle*

## 1. INTRODUCTION

In order to build a sustainable energy-oriented society, development of new energy friendly to the environment is desired. Especially the hydrogen is noticed as a next clean energy [Hydrogen and Fuel Cell Handbook Editing Committee, 2006; Honma, 2003; Koseki, 2005; Iwabuchi, 2005; Tange, 2005; Satomi, 2005; Akamatsu, 2005].

Because a fuel-cell vehicle (FCV) does not discharge harmful gas it has gotten a lot of attention recently as an eco-friendly vehicle. The safe and appropriate hydrogen source is necessary for the diffusion of a fuel-cell electric vehicle.

It is necessary to generate hydrogen by some methods, because it does not exist as resources naturally. The reforming of fossil fuel that is one of the methods for generating hydrogen is excellent in the economical efficiency. The combustion of hydrogen generates only water, but $CO_2$ eventually arises in the reforming process from fossil fuel. That is, the reforming methods are not solutions of the fundamental energy problems, because they are essentially identical to consumption of the petroleum, natural gas and so on.

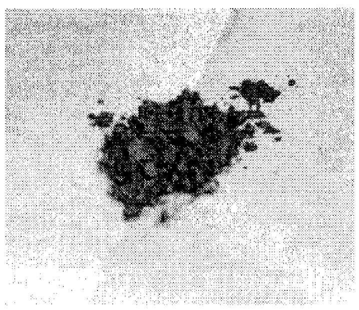
Watanabe et al. [Watanabe, 2007, Watanabe et al., 2007] propose the hydrogen production technology by the reaction between activation aluminum particles and water. The activated aluminum particles are made from sawdust which is industrial waste. They can generate pure hydrogen and change oxidized aluminum as vice-generative productions. The activated aluminum particles are able to be carried on safely, because they are stable.

However, the details of the reaction profile are yet not well known. The reaction profile should be brought out and be controlled from a practical application standpoint. Here, in this study, time changes of hydrogen generation are measured under various conditions [Takahara et al., 2008]. Secondary, the dynamic characteristics of the hydrogen generation is assumed to be described as an ARMA model [Maekawa et al., 2008]. The parameters of this model are identified using the measured results by an adaptive theory. Furthermore, the application possibility as a hydrogen source of FCV of activation aluminum is considered.

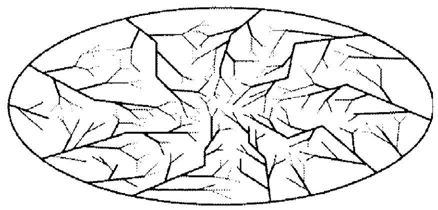
## 2. MATERIALS AND METHODS

### *2.1 Activated aluminum particles and hydrogen generation*

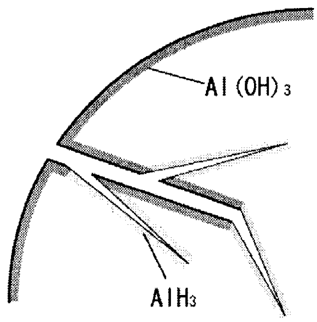
The activated aluminum particles are produced by the



(a) Activated aluminum particles



(b) Nano-cracks in activated aluminum particles




(c) Enlarged illustration of nano-cracks

**Fig. 1** Activated aluminum particles

following processes. Firstly, shredded aluminum sawdust are compressed and destroyed by a millstone at 20 ìm or less in cold water. Many micro-cracks are produced inside the microparticulated aluminum. Secondary, the aluminum particles are preserved in cold water in a week after temperature shock of about 40 degree is applied. These processes are called "activation treatment". The activation treatment makes the micro-cracks grow nano-cracks. Figure 1 shows the activated aluminum particles diagrammatically. The cross-section diagram of activated aluminum particles and the enlarged illustration of nano-crack are illustrated in (b) and (c) of Figure 1, respectively. As shown in Figure1 (c), $AlH_3$ is produced around the tip of nano-crack and expand along the each crack by corrosion reaction [Markus, 1974].
Hydrogen is generated by water decomposition. However, the reaction is not surface oxidation of aluminum [Watanabe et al., 2007]. There are countless nano-cracks in the activated aluminum particle as presented above. Water enters these cracks and water decomposition occurs. Around the tips of cracks, water decomposition is accelerated by a mechanochemical reaction and aluminum hydride $AlH_3$ is created. Nano-cracks expand along the aluminum hydride and water decomposition is accelerated furthermore.
These reactions are summarized as follow chemical formula.

$$2Al+3H_2O \rightarrow Al_2O_3+3H_2 \qquad (1)$$

One gram of the activated aluminum particles can generate 1.35 liters of pure hydrogen under the condition of 1atm and 25 degree, in theory. In fact, about one liter of hydrogen is obtained from one gram of the activated aluminum particles.
This reaction is temperature-dependent and exothermic reaction. Therefore, there is a possibility that the heat of reaction causes the explosive hydrogen generation, if the reaction temperature is not appropriately set.
In the next section, the characteristics of hydrogen generation will be measured using produced experimental system under various conditions.

### *2.2 Measurement of hydrogen generation*

In this study, the experimental system is constructed as shown in Figure 2, which can measure the temperature and pressure of the reaction online. The experimental system is separated into the primary side and the secondary side by the regulator. The left side of this figure is the primary side, and an air tight container is the hydrogen generator. The right side is secondary side, and there is a storage vessel for the generated hydrogen. The temperatures and the pressures of the primary and secondary side are respectively measured, are saved in the computer online. The hydrogen generation is calculated based on Boyle-Charle's law using the data of pressure and temperature.

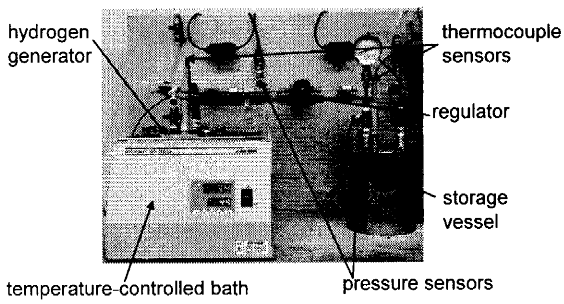



**Fig. 2** Experimental system

### *2.3 Identification of hydrogen generation*

The hydrogen generations from water and the activated aluminum particles show different characteristics according with the different of sample and experimental conditions such as the reaction temperature, water dosage,

the external temperature and so on. Therefore, it is not easy to recognize its characteristics completely. However, some appropriate description of the controlled object is necessary to synthesize a control system. The reaction rate is conceivable to nonlinearly depend on the temperature, because the reaction is mechanochemical reaction as above. Therefore, if the control system is synthesized using parameters based on measured data under a certain condition, there is a possibility that it cannot sufficiently deal with the changing reaction profile from hour to hour.
An adaptive control method is effective, in cases when the characteristics of the controlled object and/or its changes are not recognized completely.
In this study, the hydrogen yield is regarded as the output $y(k)$ of the controlled object, the hydrogen generation reaction. And the reaction temperature is regarded as its input $u(k)$. The dynamic characteristics of the hydrogen generation are assumed to be expressed by the following auto-regressive moving average (ARMA) model.

$$A(z^{-1})y(k) = B(z^{-1})u(k) \tag{2}$$

Where,

$$A(z^{-1}) = 1 + \sum_{i=1}^{n_a} a_i z^{-i}, B(z^{-1}) = \sum_{j=d}^{n_b} b_j z^{-j}$$

A mathematical model is given by

$$\begin{aligned} y_M(k) &= -\sum_{i=1}^{n_a} \hat{a}_i(k) y(k-i) + \sum_{j=d}^{n_b} \hat{b}_j u(k-j) \\ &= \hat{\boldsymbol{\theta}}^T(k)\zeta(k) \end{aligned} \tag{3}$$

Where,

$$\hat{\boldsymbol{\theta}}^T(k) = [-\hat{a}_1(k), \cdots, -\hat{a}_{n_a}(k), \hat{b}_d(k), \cdots, \hat{b}_{n_b}(k)]$$
$$\zeta^T(k) = [y(k-1), \cdots, y(k-n_a), u(k-d), \cdots u(k-n_b)]$$

The adaptive law is given by the following method called "constant trace algorithm" [Shinnaka, 1990].

$$\hat{\boldsymbol{\theta}}(k) = \hat{\boldsymbol{\theta}}(k-1) + \boldsymbol{\Gamma}(k-1)\zeta(k)\varepsilon(k) \tag{4}$$

$$\varepsilon(k) = \frac{y(k) - \hat{\boldsymbol{\theta}}^T(k-1)\zeta(k)}{1 + \zeta^T(k)\boldsymbol{\Gamma}(k-1)\zeta(k)} \tag{5}$$

$$\boldsymbol{\Gamma}(k) = (1/\lambda(k))\boldsymbol{\Gamma}'(k) \tag{6}$$

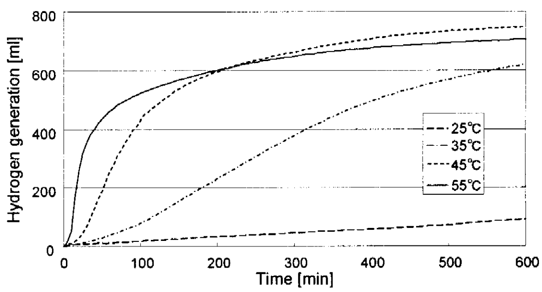
$$\begin{aligned} \boldsymbol{\Gamma}'(k) &= \boldsymbol{\Gamma}'(k-1) \\ &\quad - \frac{\boldsymbol{\Gamma}(k-1)\zeta(k)\zeta^T(k)\boldsymbol{\Gamma}(k-1)}{1 + \zeta^T(k)\boldsymbol{\Gamma}(k-1)\zeta(k)} \end{aligned} \tag{7}$$

$$\lambda(k) = tr\boldsymbol{\Gamma}'(k) / tr\boldsymbol{\Gamma}'(0), \qquad tr\boldsymbol{\Gamma}(0) > 0 \tag{8}$$

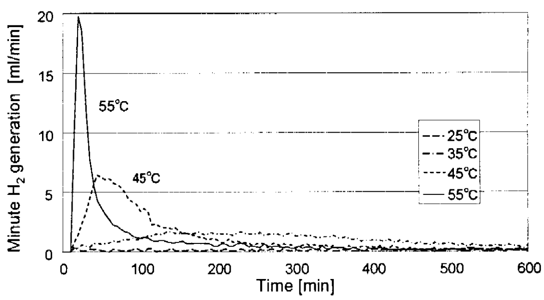
The mathematical model is innovated by the adaptive law, monitoring the reaction temperature and hydrogen yield. Thus, the non-linearity of the hydrogen generation and its characteristic changes are regarded as deviations of the parameters of the mathematical model [Wakamatsu et al., 1984].
In the next chapter, the hydrogen generation reaction will be identified as an ARMA model by the adaptive algorithm.

## 3. EXPERIMENTS

Firstly, the temperature dependency of the reaction was measured. Figures 3 shows examples of time variation of hydrogen yield in respectively with the temperature set at 25 degree, 35 degree, 45 degree and 55 degree by adding one gram of the activated aluminum particles to 20ml of water. At any temperature, total hydrogen yield were almost equal value. The results show that the hydrogen yield rate is larger and the reaction is quicker, as the temperature is higher.



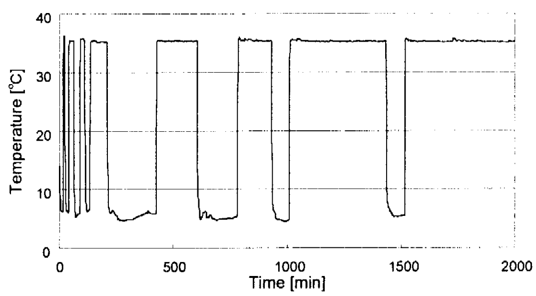

(a) Hydrogen generation



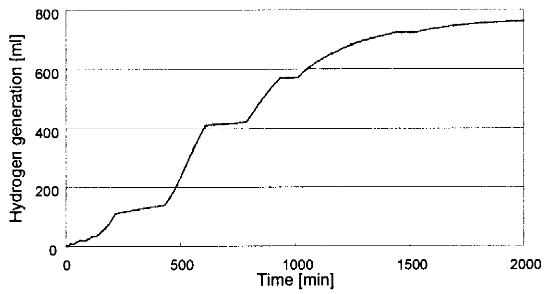

(b) Minute hydrogen generation

**Fig. 3** Temperature dependence of hydrogen generation

Furthermore, the change of the hydrogen yield was measured, when the reaction temperature was randomly changed like pulse. Figure 4 shows the measured result. This result shows that the hydrogen yield rate




(a) Reaction temperature

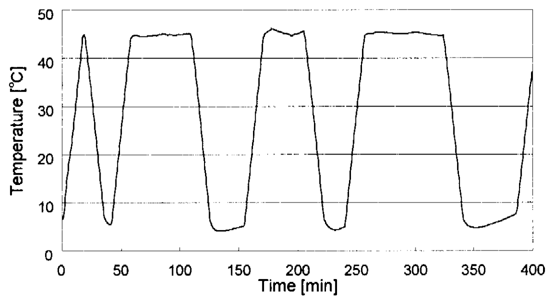



(b) Hydrogen generation

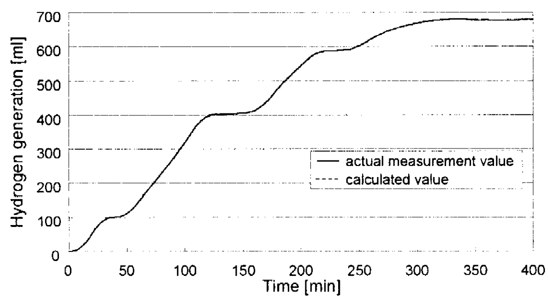
**Fig. 4** Hydrogen generation for the changes of reaction temperature

changes due to the temperature in the hydrogen generator. The total hydrogen yield was equal to the total yield under the condition of constant temperature. That is, the temperature control is conceivable to be one of the effective methods for controlling hydrogen generation, because the change of the temperature does not affect the total hydrogen yield. The low temperature of about 5 degree, the reaction become suppressed but not stopped.

The parameters of the above ARMA model were identified using the measured data. Here, the parameters of the memory length and dead-time are chosen as $n$=2, $m$=1 and $d$=1, respectively. Figure 5 shows the identification result. Figure 5 (a) and (b) are the change of reaction temperature and hydrogen yield, respectively. In the same figure (b), the output of mathematical model drawn in dotted line is roughly in accordance with the measured value drawn in continuous line. The largest identification error is 5% around the start of identification. Therefore, the ARMA model is conceivable to describe the hydrogen generation characteristic for control.




(a) Reaction temperature




(b) Hydrogen generation

**Fig. 5** Identification using a linear ARMA model

## 4. APPLICATION POSSIBILITY TO A FUEL-CELL ELECTRIC VEHICLE

The follows are required as a hydrogen source for automobile use.

(1) safety
(2) lightweight properties
(3) compactness
(4) user-friendliness

A high-pressure storage tank of hydrogen is one of the hydrogen storage methods in FCV. A C-FRP container is liner made by aluminum alloy reinforced in carbon fibre reinforced plastic. It is superior in terms of lightweight properties because its vessel weight per unit inner volume is about 0.3 [kg/*l*]. Increase of the pressure of the stored hydrogen is needed because increase of the mileage is demanded to give FCV convenience like a gasoline car. Liquid hydrogen can be transported and stored by big mass energy density compactly. However, handling of such a high pressure tank is always accompanied with danger of fire and explosion. Furthermore, a system to reduce evaporative loss from a container is needed to store up liquid hydrogen.

The activated aluminum is easy to handle because is can produce pure hydrogen simply by adding water. Even if a high-pressure storage tank has the high strength that does not fail in an accident, the destruction of the flow control valve hydrogen leak from the tank. In the case of the system using the activated aluminum particles, the destruction of the reactor vessel only produce oxidation of the activated aluminum particles. Therefore, it is thought that the activated aluminum particles have higher safety than the high-pressure storage tank.

The metal hydride can store up hydrogen storage density per the unit volume highly. It has high safety with a compact but is heavy and expensive. The maximum inventory quantity of practical metal hydride is 1.4 % by weight in LaNi5, is 3.6 % by weight in Mg2Ni. On the other hand, the storage quantity of the activated aluminum particle is 11.2 % by weight theoretically and is 8.9 % by weight based on the measured value. For example, the tank of activated aluminum particles to get 450 [*l*] of hydrogen is almost the same size as MHCh-450L [The Japan Steel Works, 2008.] which is made of a hydrogen storage alloys for FCV (The Japan Steel Works Ltd.), and the weight of activated aluminum particles is about a one-tenth of the hydrogen storage alloys. That is, it is conceivable that the use of activated aluminum particles enables light-weighting.

Therefore, it is thought that the activated aluminum particles are suitable as fuel for FCV.

## 5. CONCLUSIONS

In this study, the hydrogen generation from water decomposition with the activated aluminum particles was measured. It was confirmed the temperature dependency of the reaction. The characteristics of the hydrogen generation showed a different value depending on a sample and an outside condition quantitatively, but agreed qualitatively. The reaction was assumed to be described as a linear ARMA model, where, the input and output variables were the reaction temperature and the hydrogen generation, respectively. The characteristics of the reaction were identified as the ARMA model using the measured data. It was confirmed that the output value of the mathematical model accorded with the actual measured data well. Therefore, the linear ARMA model is conceivable to describe the hydrogen generation characteristic for control. Furthermore, the application possibility as a hydrogen source of FCV of activation aluminum is considered by comparison with the other storage methods.

The construction of the system to control the hydrogen generation is an issue in the future

## Acknowledgement

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