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## 고체 상태 NaBH4 수소발생 및 연료전지 무인기 시스템 적용 연구

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Study on hydrogen generation from solid-state NaBH<sub>4</sub> for fuel cell unmanned aerial vehicle application

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#### ABSTRACT

#### Study on hydrogen generation from solid-state NaBH<sub>4</sub> for fuel cell unmanned aerial vehicle application

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최근 많은 국가 및 연구소에서 무인기의 체공시간을 증가시키기 위해 다 양한 연구가 진행 중이다. 무인기의 체공시간을 증가시키기 위해 제일 먼저 접근하는 방법은 동력원에 대한 개선이다. 무인기의 동력원으로 사용되고 있 는 내연기관 및 화석연료는 상용화가 되어있는 장점이 있지만, 내연기관은 에너지 변환과정에서 발생하는 에너지손실에 의한 한계와 화석연료에서 배 출되는 오염물질로 인해 2차 전지를 이용한 방식으로 대체하고 있다. 하지만 2차전지의 경우 위에서 언급한 내연기관의 문제를 개선할 수 있지만, 에너지 밀도를 증가시키기는 것에 한계가 있어 무인기의 체공시간을 증대시키기에 는 적합하지 않다. 따라서 이러한 2차전지의 문제점을 해결하고자 다양한 연 구가 진행 중이다. 그 중 연료전지는 2차전지보다 에너지밀도가 높은 장점이 있으며 화학적 에너지를 전기적 에너지로 직접 변환하기에 에너지 변환 효 율이 높은 장점이 있다. 이러한 장점을 가진 연료전지를 무인기의 동력원으 로 적용하면 기존의 제한된 무인항공기의 체공시간을 증가시킬 수 있다. 연 료전지의 에너지밀도를 결정하는 것은 연료전지 자체가 아닌 연료전지의 연 료인 수소를 저장 및 공급하는 방식을 합쳐서 결정된다. 따라서 수소 저장 및 공급 방식을 연료전지를 적용한 무인기의 목적에 맞게 사용해야한다. 수 소를 저장하는 방식에는 압축, 액화, 금속수소화물, 화학수소화물 등 다양한 방식이 있다. 그 중 화학수소화물은 상온에서 고체상태로 저장되기에 운반 및 취급에 용이한 장점이 있으며, 다양한 화학수소화물중 NaBH4는 10.6 wt.%라는 높은 수소저장밀도를 가지는 장점이 있다. 이러한 수소 저장 밀도 는 연료전지의 에너지밀도를 더욱 증가시킬 수 있는 요인이기에 본 연구에 서 수소 저장 및 공급원으로서 선정하였다. NaBH4에서 수소를 발생시키는 방법에는 NaBH₄ 수용액과 촉매를 이용한 방식이 있다. 하지만 이러한 방식 은 NaBH4 용해도 문제와 장기간 저장이 어려운 단점이 있어 연료전지 에너 지밀도를 증가시키는 데에는 적합하지 않다. 따라서 기존에 선행 된 연구인 고체상태의 NaBH4에서 HCl 수용액을 사용하여 직접 수소를 분해시키는 방 법을 사용하였다. HCl 수용액을 이용하여 NaBH4를 직접 분해하면 빠른 수소 발생 특성과 NaBH4 수용액의 문제점을 해결할 수 있지만, HCl의 낮은 pH에 의한 특성으로 부식에 대한 문제가 있다. 이 문제를 개선하기 위해 HCI 수 용액에서 N 농도를 감소시키면 반응에 기여하지 않는 과량의물 증가로 수소 발생효율이 감소하게 된다. 즉 저장된 수소양 대비 발생된 수소양이 감소하 기에 에너지밀도가 감소하게 된다. 이러한 문제를 해결하기 위해 본 연구에 서는 HCl 수용액이 NaBH4와 반응하면 NaCl로 결합되는 특성과 HCl 수용액 에서 반응에 기여하지 않는 과량의 물 개선하기 위해 CoCl,를 HCl 수용액에 첨가하여 분해제를 조성하였다. 조성한 분해제를 바탕으로 NaBH₄ 수소발생 실험을 진행하였으며, 실험결과를 서술 하였다.



#### I. Researching background

Many countries and research institutes are developing Unmanned Aerial Vehicle(UAV) for aerial recon purpose. The aerial recon mission of a UAV is reconned a specific area using an observation device and precision communication device. The important factor in determining a UAV recon mission success is the UAV duration of the flight. As the UAV duration of the flight increases is mean aerial recon time increases, so the UAV duration of the flight is an important factor in determining mission success. Therefore, power units of UAV are studying to increase the flight time of UAV. The commercial power units of UAV are combustion engines using fossil fuel and electric power that combined the secondary battery with the motor. Among then, combustion engines have a problem with fossil fuel depletion and environmental pollution by fossil fuel combustion. On the contrary, the power unit using electric motor has advantages eco-friendly because less noisy and not generated environmental pollution like fossil fuel. Therefore, Due to the problem of the combustion engine, the combustion engine of UAV is being replaced electrical power unit that combined electrical motor and secondary battery. However, the secondary battery is not sufficient as a power source for increasing the UAV duration of the flight. The reason why the secondary battery is not sufficient for the power source of UAV is that gravimetric energy density is low than 200 W • hr/kg [1]. The gravimetric energy density of the secondary battery is not sufficient to extend the duration of the flight. Therefore, many researchers are studying other power sources that higher than 200 W • hr/kg of gravimetric energy density. The fuel cell has a higher gravimetric energy density than the secondary cell, and eco-friendly advantages to useing hydrogen. Also, the fuel cell has a high energy efficiency since it converts chemical energy directly into electrical energy. For this reason, the fuel cell is recognized as the most promising power source that can be an alternative to the secondary battery [2].



However, the fuel cell itself does not have an energy density, it generates energy using hydrogen as Fig. 1. In other words, the energy density does not calculate by only the fuel cell, the energy density of the entire fuel cell system is calculated including hydrogen supplying and stored device. The energy density is defined as the ratio of the energy capacity the total system weight. Thus two ways to improve the energy density can be considered one is to increase the energy capacity and the other is to reduce the entire system weight. Fig. 2 is a layout of fuel cell that consists of hardware and stacking method. The entire fuel cell is consisted Membrane Electrode Assembly(MEA), bipolar plate, end plate, gas channel, and cooling fan. The first simple approach is to reduce the weight of the components of the fuel cell system. However, The reduce the weight of fuel cell are difficult because it has a limit about component material property and stacking method. For this reason, many research projects have been conducted focusing on the improvement of the hydrogen storage and supplying method using such technical approaches. In the fig. 2 described various hydrogen storage and supply methods. Typically, compressed hydrogen [3], liquified hydrogen [4], metal hydride [5] and chemical hydride [6] storages are used to fuel cell systems for hydrogen storage and supply. The compressed and liquified hydrogen storage methods require equipment for liquefaction and compression to refill the hydrogen. The refueling should also ideally be performed in a separate location. Metal hydride is easy to refill, but its associated gravimetric hydrogen storage density is much lower than that associated with the other methods [7], So it is not suitable for portable and aeronautical applications [8]. Unlike the aforementioned hydrogens storage methods, the chemical hydride is easy and safe to handle and also possesses a relatively high hydrogen storage density. These merits in particular, set chemical hydride apart as a promising hydrogen storage method for UAV applications [9]. Among the chemical hydride, The sodium borohydride(NaBH<sub>4</sub>) has high hydrogen storage density of 10.6 wt% than other chemical hydrides.



The aforementioned merits are NaBH<sub>4</sub> aqueous solution and catalyst reaction [10]. The fig. 4 is a NaBH<sub>4</sub> aqueous solution based fuel cell power pack [11]. However, the critical problem was encountered regarding the low yield rate and unstable storage. Recently, direct hydrogen generation methods using NaBH<sub>4</sub> in the solid-state have been studied in order to solve the aforementioned problems and improved energy density [12]. Several methods are available for generating hydrogen from NaBH<sub>4</sub> They are typically all based on hydrolysis, while acid [13], steam [14], and catalyst[15] have been used to accelerate the hydrolysis process. In general, many catalysts such as Ru, Co, Ni, and their combinations have been used to generate hydrogen from NaBH<sub>4</sub>, but they are typically problematic in terms of reliability and durability. The steam method has the disadvantage of considering the device for vaporizing and the power consumption for vaporizing. The NaBH<sub>4</sub> decomposition using acid improve the disadvantage of other hydrogen generation methods since acid has a characteristic of accelerated decomposing NaBH<sub>4</sub>, so the hydrogen generation method using solid-state NaBH<sub>4</sub> with acid has been studied for application to fuel cell UAV. A variety of acids are able to accelerate NaBH<sub>4</sub> decomposition such as hydrochloric acid(HCl) [12], Acetic acid(CH<sub>3</sub>COOH) [16], Formic acid(HCOOH) [17]. Among them, an HCl solution was selected as a hydrogen generation agent because its associated accelerated hydrogen generation rate was higher than that associated with other acids [12]. However, the component such as pump, tube, and fitting are damaged by corrosion since the low pH of HCl. also, Since HCl aqueous solution is composed by adding water to HCl, an unnecessary amount of water that is not required for the NaBH<sub>4</sub> reaction is added. unnecessary water in the NaBH<sub>4</sub> reaction must be reduced for improvement gravimetric energy density and reaction ratio because energy density decreasing is affected by unnecessary water increasing. Thus, in this paper, chloride compound powder was added to the HCl solution in order that improvement the unnecessary water in the reaction.



Cobalt Chloride (CoCl<sub>2</sub>), which is widely used in the catalysts among various chloride compounds and has excellent performance as a NaBH<sub>4</sub> aqueous solution catalyst, was selected [10]. In this study, the decomposing agent that combination HCl aqueous solution and CoCl<sub>2</sub> was reacted with NaBH<sub>4</sub> to compare the hydrogen generation rate, Agent/NaBH<sub>4</sub> reaction ratio and the amount of water not participating in the reaction. Finally, based on the results the CoCl<sub>2</sub> + HCl agent for NaBH<sub>4</sub> decomposition was described the energy density improvement and applicability of fuel cell UAV in this paper.



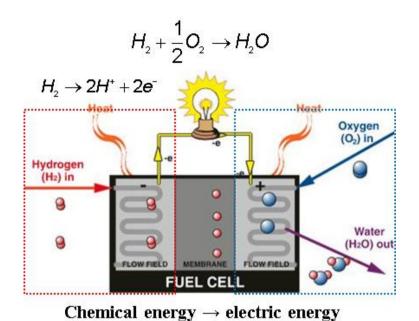


Fig. 1 Operation mechanism and layout of Fuel-cell

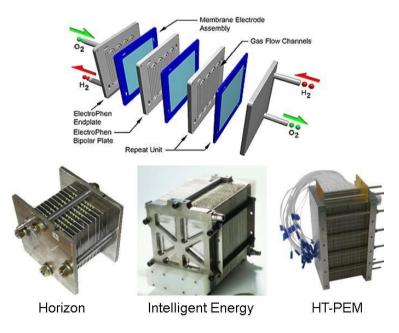


Fig. 2 Configuration of Polymer Electrical Membrane Fuel-cell



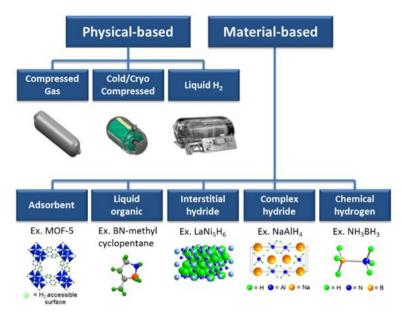


Fig. 3 Various hydrogen storage and supply methods for Fuel-cell



Fig. 4 The NaBH<sub>4</sub> Solution-based all in on Fuel cell power pack



# □. NaBH<sub>4</sub> pH characteristics and hydrogen generation method

#### 1. NaBH<sub>4</sub> pH half-life and NaCl bond

Figure 5 is solid-state NaBH<sub>4</sub> in room condition. The NaBH<sub>4</sub> is a type of chemical hydride in which Natrium(Na), Boron(B), Hydrogen(H) elements are combined such as Fig. 6. The method of generating hydrogen from NaBH<sub>4</sub> is the same as that decomposing hydrogen from bonded NaBH<sub>4</sub>. Typically, a method of decomposing hydrogen from NaBH<sub>4</sub> is hydrolysis using water. The define of hydrolysis is any chemical in which a molecule of water decomposed one or more chemical bonds. Therefore, when reaction 1 mole of NaBH<sub>4</sub> with 2 moles of H<sub>2</sub>O are generated 1 mole of NaBO<sub>2</sub>, 4 moles of H<sub>2</sub>, and reaction Heat by Eq. (1). However, Eq. (1) is stoichiometric what is not considered actual condition and reaction parameters. It means that hydrogen generation efficiency and response is not enough for hydrogen generation method. To solve this problem, decomposition characteristics of NaBH<sub>4</sub> according to the ambient pH environment are used as shown in Table 1 [12].

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 + Heat \tag{1}$$

In table 1, the  $NaBH_4$  decomposition accelerates up to 0.0037 seconds when the pH is decreased. On the contrary, the  $NaBH_4$  decomposition delays up to 426.2 days when the pH is increased.



Typically, the hydrogen generation methods from NaBH<sub>4</sub> using pH characteristic is NaBH<sub>4</sub> aqueous solution and catalyst reaction [10]. The NaBH<sub>4</sub> aqueous solution should be kept at a high pH by adding an alkaline chemical such as sodium hydroxide(NaOH) since NaBH<sub>4</sub> reaction is hydrolysis using water. However, NaBH<sub>4</sub> aqueous solution methods have a serious problem that NaOH added to maintain NaBH<sub>4</sub> aqueous solution does not participation in the reaction as shown in Eq. (2). It means hydrogen storage density decrease. Also, even if NaOH is added to maintain high pH, the long-term storage of NaBH<sub>4</sub> aqueous solution is problematic because it delays the decomposition time as shown in Table 1.

$$NaBH_4 + (2H_2O + xNaOH) \rightarrow NaBO_2 + xNaOH + 4H_2 + Heat$$
 (2)

Another problematic of NaBH<sub>4</sub> aqueous solution is related to hydrogen generation performance using a catalyst. The hydrogen yield-rate of the catalytic method is not high enough and is too unstable because catalytic performance is varied by temperature and environment. Moreover, catalytic degrading of what related to loss and surface adsorption of NaBO2 is consistently decreases hydrogen generation performance [12]. To increase the hydrogen storage density of  $NaBH_4$  aqueous solution, the amount of water and NaOH should be minimized and the amount of NaBH<sub>4</sub> should be increased. But it is hard to increase the hydrogen storage density of NaBH<sub>4</sub> aqueous solution because of NaBH<sub>4</sub> solubility problem. In order to solve the problem of NaBH<sub>4</sub> aqueous solution method, Lee et al. studied hydrogen generation method using a hydrochloric acid the solution of characteristic that solid-state NaBH<sub>4</sub> is accelerated decomposed at low pH as shown in Table 1 [13].





Fig. 5 solid-state sodium borohydride at room condition

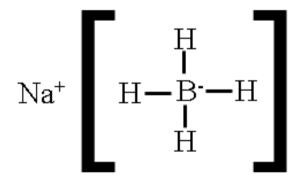


Fig. 6 Molecular structure of solid-state NaBH<sub>4</sub>



The NaBH<sub>4</sub> exists in the solid-sate at room condition so it is promised long-term storage. also, the aforementioned catalytic problem is improved using a hydrochloric acid solution that solid-state NaBH<sub>4</sub> agent solution. The chemical reaction of solid-state NaBH<sub>4</sub> and HCl aqueous solution is Eq. (3)

$$NaBH_4 + (HCl + 3H_2O) \rightarrow NaCl + H_3BO_3 + 4H_2 + Heat$$
(3)

The equation (2) and (3) has different by-product after the hydrolysis reaction. In eq (2), NaBH<sub>4</sub> when after reaction generates NaBO<sub>2</sub> as a by-product, whereas in eq (3) NaBH<sub>4</sub> generates Sodium Chloride (NaCl) as a by-product. The chemical reaction of solid-state NaBH<sub>4</sub> and CoCl<sub>2</sub> solution are Eq. (4) [18]. The CoCl<sub>2</sub> aqueous solution reacts with NaBH<sub>4</sub> to produce NaCl and Cobalt boride (Co<sub>2</sub>B) as by-products. In other words, the low pH of the HCl aqueous solution has accelerated decomposition of NaBH<sub>4</sub>, and then combine the cation Na<sup>+</sup> and the anion Cl<sup>-</sup> are produce NaCl. on the contrary, eq. (4) means that NaBH<sub>4</sub> is reacted with a CoCl<sub>2</sub> aqueous solution so that NaCl combination from the cation Na<sup>+</sup> and the anion Cl<sup>-</sup>. As a result, the reaction of solid-state NaBH<sub>4</sub> and Cl aqueous solution are generated hydrogen since the NaCl bond. [18].

$$2CoCl_2 + 4NaBH_4 + 9H_2O \rightarrow Co_2B + 4NaCl + 12.5H_2 + 3B(OH)_3$$
(4)



pН	NaBH <sub>4</sub> Half-life
4.0	0.0037 sec
5.0	0.037 sec
5.5	0.12 sec
6.0	0.37 sec
7.0	3.7 sec
8.0	36.8 sec
9.0	6.1 min
10.0	61.4 min
11.0	10.2 hours
12.0	4.3 days
13.0	42.6 days
14.0	426.2 days

Table 1. Half-life of Solid-state NaBH<sub>4</sub> according to pH environment

Table 2 Hydrogen generation rate of NaBH<sub>4</sub> from HCl different Normality

HCl (N)	Generation H <sub>2</sub> (ml)	H <sub>2</sub> yield(%)
2.5	47,298	91.9
3	48,928	95.0
3.5	48,122	93.5
4.0	46,268	89.9



# 2. The composition of agent solution for solid-state NaBH<sub>4</sub> decomposition

Combining the Eq. (2) and Eq. (3), the overall hydrolysis reaction using the HCl solution is expressed in Eq. (5). where x should be 0 < x < 1. If x is 0, the reaction corresponds to Eq. (2), and if x is 1, it corresponds to Eq. (3). In addition, the x is a factor determining the concentration of the HCl solution, on which the reaction rate of NaBH<sub>4</sub> hydrolysis is strongly dependent.  $\alpha$  is the excess water not contributing to the hydrogen generation reaction, which should be minimized to improve hydrogen storage density. The method of reducing  $\alpha$  in aqueous HCl solution increase the reaction efficiency with NaBH<sub>4</sub> or increase the HCl normality(N).

$$NaBH_4 + xHCl + (x + \alpha + 2)H_2O \rightarrow$$

$$xNaCl + xH_3BO_3 + (1 - x)NaBO_2 + \alpha H_2O + 4H_2$$
(5)

Increasing the HCl normality in aqueous HCl solution reduces the water that added in the HCl aqueous solution. Therefore, excess water  $\alpha$  in HCl aqueous solution is decreased. However, increasing HCl normality is accelerated HCl vaporization and decreases BOP durability by corrosion. also, the hydrogen generation efficiency of solid-state NaBH<sub>4</sub> and HCl aqueous solution reaction decreases at HCl 4N as shown in Table 2. Decreasing the HCl normality in aqueous HCl solution increases the water that added in the HCl aqueous solution. Increasing water of added in the HCl aqueous solution is decreased hydrogen generation efficiency since decreasing HCl normality as shown in table 2. As a result, the method of increasing the normality of HCl in the HCl aqueous solution does not suitable what increases the hydrogen storage density.[13].



Thus, the  $CoCl_2$  was added to HCl aqueous solution for improved the reaction efficiency and excess water in this study. as shown in Eq. (4), the CoCl<sub>2</sub> aqueous solution and solid-state NaBH<sub>4</sub> reaction are generated NaCl and hydrogen as a by-product. In Eq. (4), The hydrogen mole generated by the reaction of 1 mole NaBH<sub>4</sub> with 0.5 mole CoCl<sub>2</sub> is 3.125 mole, which is 0.875 moles lower than  $H_2$  mole in Eq. (3). The decomposing solid-state NaBH<sub>4</sub> with CoCl<sub>2</sub> aqueous solution is not suitable for improving reaction efficiency and excess water. Therefore, agent solution for solid-state NaBH<sub>4</sub> composition was combined HCl aqueous solution that has characteristics accelerated decomposition and high hydrogen generation efficiency, with CoCl<sub>2</sub> has an NaCl reaction. Combining the Eq. (3) and Eq. (4), the overall hydrolysis reaction using the HCl solution and  $CoCl_2$  solution is expressed in Eq. (6). In Eq. 3, the y is the mole of  $CoCl_2$ , and the range is 0 < y < 1. If y is 0, the reaction of Eq. (6) corresponds to Eq. (5), and if y is 1 and x is 0, the reaction corresponds to Eq (4). Based on Eq. (6) the solid-state  $NaBH_4$  agent solution was composed to find out optimization ratio as shown in table 3

$$NaBH_{4} + xHCl + \frac{y}{2}CoCl_{2} + (x + \frac{5}{2}y + \alpha + 2)H_{2}O \rightarrow (x+y)NaCl + [1 - (x+y)]NaBO_{2} + \frac{y}{2}Co_{2}B + (x + \frac{3}{4}y)H_{3}BO_{3} + \alpha H_{2}O + (4 - 0.875y)H_{2}$$
(6)



HCl (N)	CoCl <sub>2</sub> (wt.%)
	0
	5
1	10
	15
	20
	0
	5
-	10
2	15
	20
	0
	5
2	10
3	15
	20

#### Table 3 Agent composition for solid-state NaBH<sub>4</sub> direct decomposition



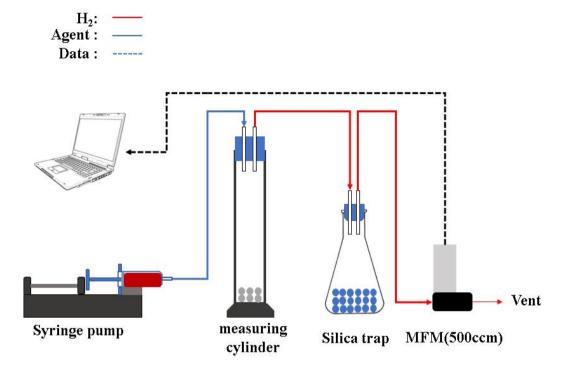


Fig. 7 Experiment set-up of NaBH<sub>4</sub> Hydrogen generation using Mass Flow Meter

# III. The solid-state NaBH<sub>4</sub> decomposition experiment using agent solution

## 1. The NaBH<sub>4</sub> decomposition experiment set-up using MFM and experiment result

The experiment of solid-state NaBH<sub>4</sub> decomposition using agent solutions was configured as shown in Fig. 7. In Fig 7, The agent solution was injected to solid-state NaBH<sub>4</sub> using the syringe pump, and solid-state NaBH<sub>4</sub> reacted with agent solution. after the hydrolysis reaction, the hydrogen flow rate was measured through the MFM. Using the aforementioned experiment method, the NaBH<sub>4</sub> decomposition experiment was conducted based on Fig. 7 for the understanding of the characteristics of HCl and  $CoCl_2$  solution when reacted with 1 g of NaBH<sub>4</sub>. The experimental results of decomposing hydrogen in NaBH<sub>4</sub> using HCl 3N aqueous solution and CoCl<sub>2</sub> 5wt% solution were described in Fig. 8 and Fig. 9. As shown in Fig 8, the hydrogen was immediately decomposed from NaBH<sub>4</sub> when HCl 3N aqueous solution is injected into the NaBH<sub>4</sub> surface once by a syringe pump. on the contrary, Although CoCl<sub>2</sub> 5wt.% aqueous solution was injected on the NaBH<sub>4</sub> surface, the hydrogen was gradually decomposed after 143 seconds without decomposed during 143 seconds. Fig. 10 is a graph decomposed NaBH4 using CoCl<sub>2</sub> aqueous solution in which the additional amount of CoCl<sub>2</sub> increased to 10 wt%. The NaBH<sub>4</sub> decomposition start time was 78 seconds faster than CoCl<sub>2</sub> 5 wt% aqueous solution since the amount of CoCl<sub>2</sub> added increased from 5 wt% to 10 wt%. The CoCl<sub>2</sub> 10wt% aqueous solution decomposes NaBH<sub>4</sub> and generates hydrogen in constantly, but the hydrogen at between 124 and 130 seconds do not measure since over the MFM maximum measurement of 550 Standard Cubic Centimeters per Minute (SCCM). The difference between the hydrogen decomposition result of fig. 8 and 9 are NaBH<sub>4</sub> decomposition characteristics that have accelerated decomposition at low pH of HCl, and decomposition characteristic due to NaCl bonding.



In other words, HCl 3N aqueous solution affects the NaBH<sub>4</sub> decomposition by low pH of HCl as shown in Table 1, while the CoCl<sub>2</sub> aqueous solution does not lower sufficiently the pH. As a result, NaBH<sub>4</sub> decomposition start time decreases when the amount of CoCl<sub>2</sub> added in the aqueous solution of CoCl<sub>2</sub> increases. However, it has an important issue that hydrogen generated exceed MFM maximum measurement. In other words, the aforementioned problem does not promise a reliable result. To solve the above-mentioned problem, the experimental method without MFM equipment was constructed as shown in Fig. 11.



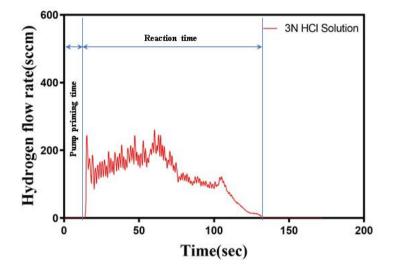


Fig. 8 Hydrogen generation rate at HCl 3N solution

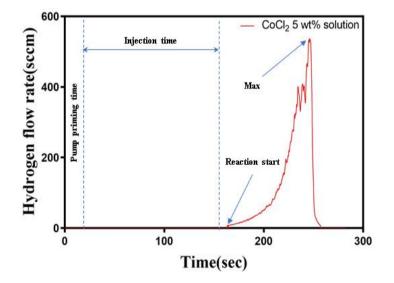


Fig. 9 Hydrogen generation rate at CoCl\_ 5wt.% solution



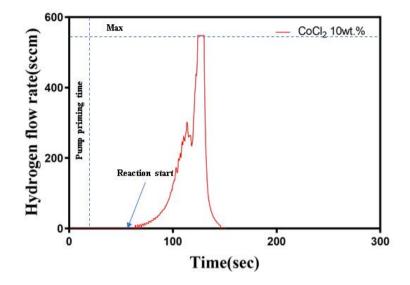


Fig. 10 Hydrogen generation rate at  $CoCl_2$  10 wt.% solution

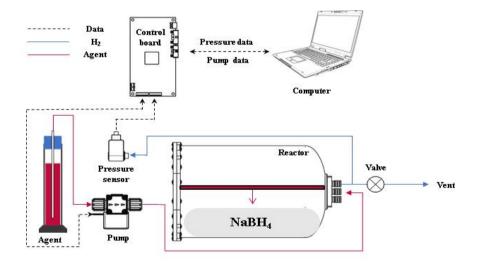


Fig. 11 The NaBH<sub>4</sub> reaction pressure based Agent composition experiment set-up



## 2. The experiment and configuration of NaBH<sub>4</sub> based reaction pressure using agent solution

Figure 11 was lay-out experimental method to solve the problems mentioned in the above section. The fig. 11 is unlike measuring methods using MFM equipment, It was consisted of a controller, reactors, pumps and pressure sensors. The reactor was designed in a sealing structure, and the pump moving the agent solution to NaBH<sub>4</sub> in the reactor and injected to NaBH<sub>4</sub> surface. The hydrogen is generated at NaBH<sub>4</sub> when reacts with the injected agent solution and pressure is generated inside the reactor because it remains sealing structure. At this time, the pressure sensor measures the pressure by generated hydrogen and transmits the data of control board to the computer through RS232 communication. The reactor pressure is the pressure that measured by the hydrogen generation, the pressure in the reactor are continuously increased when the pump is continuously operated to inject the agent solution. Since the continuously pressure increasing is damaged to reactor and un-safety, the react pressure control algorithm is applied as shown in Fig. 12. When the reactor pressure is lower than the set pressure the pump is operated to move the agent solution and injected the NaBH<sub>4</sub> to generate hydrogen by the reaction pressure control algorithm. on the contrary, after the agent solution decomposes hydrogen from NaBH<sub>4</sub>, the pump is stopped when the reactor pressure is higher than the set pressure. If the reactor pressure increased to the limit pressure, the solenoid valve was opened and vent the hydrogen by reactor pressure control algorithm.



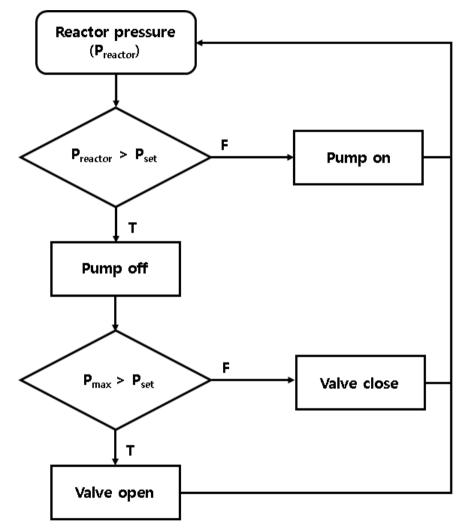


Fig. 12 Control algorithm of hydrogen pressure and solenoid valve



#### 1) The experiment method based on NaBH<sub>4</sub> reaction pressure

The purpose of the experiment in fig 11 is not to measure the hydrogen generation efficiency, it measures the consumed the agent solution when reactor pressure increased until set pressure by NaBH<sub>4</sub> decomposition. Therefore, an experiment based on NaBH<sub>4</sub> reaction pressure was prepared as follows.

First, NaBH<sub>4</sub> in the reactor was filled up to 20% of NaBH<sub>4</sub> with respect to the volume of the reactor for sufficiently react NaBH<sub>4</sub> with the agent solution. The agent solution was injected to decompose the NaBH<sub>4</sub> until the set pressure 2.1 bar. and then the consumed agent solution was measured when NaBH<sub>4</sub>decomposed to reach the 2.1 bar. At this time, the excess water that did not contribute to the reaction was calculated using the eq. (5) the amount mole of the HCl aqueous solution except the amount of CoCl<sub>2</sub> in the consumed decomposition agent solution. The 1 mole of NaBH<sub>4</sub> was assumed that was entire reacted at eq. 5. The second is a comparison of NaBH<sub>4</sub> and agent solution reaction efficiency. Using the same experiment configuration, 20g of NaBH<sub>4</sub> was reacted with each of the agent solutions until the reaction was completed, and the amount of agent solution used in the reaction was measured and calculated by Agent/NaBH<sub>4</sub> efficiency. Finally, the by-products produced from the entire reacted NaBH<sub>4</sub> were analyzed using X-ray Diffraction (XRD) method.



## 2) The experiment results of NaBH<sub>4</sub> reaction pressure using HCl aqueous solution

Figure 13 is reactor pressure experiment result measured at decomposing hydrogen in NaBH<sub>4</sub> using aqueous HCl solution. The reactor pressure are increased because NaBH<sub>4</sub> generates hydrogen in the reactor that is a sealing structure. The consumption time to reach the set pressure of 2.1 bar was decreased as the normality of HCl was increased as shown in fig. 13. Increasing the normality of HCl was increases the x value of HCl in eq. (5). In addition, the eq. (5) is correspond to eq. (3) as the normality of HCl increasing in fig. 13. Therefore, NaBH<sub>4</sub> decomposition rate are increased and minimum consumption time for reach the set pressure 2.1 bar was 0.93 minutes in 3N HCl aqueous solution. On the contrary, when the normality of HCl decreases, the xvalue are decreased since the amount of HCl added was decreased. At this time, the NaBH<sub>4</sub> decomposition rate are decreased since eq. 5 is correspond to eq. 1. The NaBH<sub>4</sub> decomposition rate are decreased and maximum consumption time for reach the set pressure 2.1bar was 1.58 minutes in 1N HCl aqueous solution. As a result, decreased consumption time for the reactor pressure to reach the set pressure are equivalent mean that the reaction efficiency of the injected agent solution and the solid-state NaBH<sub>4</sub> is increased.



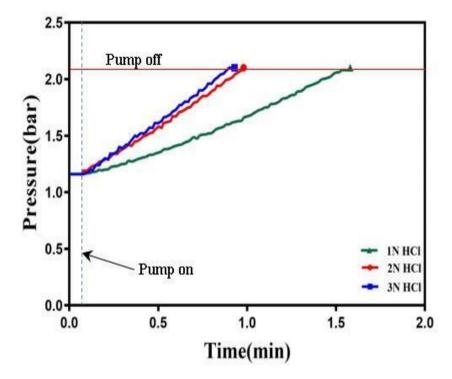


Fig. 13 Hydrogen generation pressure of HCl solutions

## 3) The experiment results of NaBH<sub>4</sub> reaction pressure based using HCl+CoCl<sub>2</sub> agent solutions

Figure 14 is the reactor pressure experiment result measured at decomposing hydrogen in NaBH<sub>4</sub> using agent solution that composition CoCl<sub>2</sub> 5, 10, 15, 20 wt.% with HCl 3N solution. When the HCl  $3N + CoCl_2$  agent solution increased from  $CoCl_2$  5wt% to 10wt%, the consumption time to reach the set pressure was reduced than the HCl 3N solution, but it is not sufficient to compared reaction efficiency. One the contrary, HCl 3N + CoCl<sub>2</sub> 20wt.% the agent was consumed 7.8 seconds more to reach the set pressure 2.1 bar than HCl 3N aqueous solution. In fig. 15, the HCl  $2N + CoCl_2$  agent solutions consumed an average of 46.8 seconds to reach the set pressure of 2.1 bar and consumed 1.28 time than the HCl 2N aqueous solution. Also, the consumption time to reach the set pressure using HCl 2N + CoCl<sub>2</sub> 20wt.% improved the 7.2 seconds than 2N HCl solution, it means that improved the excess water in 2N HCl aqueous solution using NaCl bond of  $CoCl_2$ . The HCl  $1N + CoCl_2$  agent solutions consumed an average of 48.6 seconds to reach the set pressure 2.1 bar and consumed 1.95 times less than 1N HCl aqueous solution as shown in Fig. 16. The consumption time that reaches the set pressure during the above experiment result decreased to the maximum at HCl  $1N + CoCl_2$  agent solution. Also, the reactor pressure was consistently increased, regardless of the pump does not operate by control algorithm when reaching the set pressure 2.1bar. The reason why reactor pressure consistently increased is NaBH<sub>4</sub> decomposition characteristic of CoCl<sub>2</sub> as shown in fig. 9. also, it was sufficiently improved the excess water that does not contribute to NaBH<sub>4</sub> decomposition. However, the NaCl bond characteristic of CoCl<sub>2</sub> did not sufficiently affect to the improvement of excess water in 3N HCl + CoCl<sub>2</sub> aqueous solution. because the mole value of the HCl 3N aqueous solution was sufficiently higher than  $CoCl_2$  mole vale at 3N HCl +  $CoCl_2$  agent solutions in eq. 6. So that, NaCl bond characteristic and excess water improvement were affected by HCl  $2N + CoCl_2$  agent solution which is one step lower than HCl  $3N + CoCl_2$  agent solution. Finally, the above-mentioned CoCl<sub>2</sub> NaCl bond characteristic and excess water improvement were maximized in the HCl  $1N + CoCl_2$  agent solution.



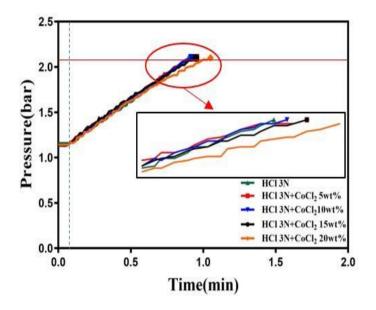


Fig. 14 Hydrogen generation pressure of HCl  $3N + CoCl_2$  agents

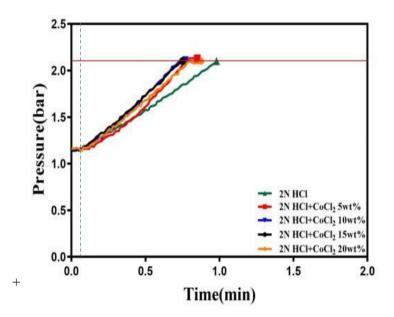


Fig. 15 Hydrogen generation pressure of HCl  $2N + CoCl_2$  agents



The measured agent solution consumed to NaBH<sub>4</sub> decomposition during the reaction pressure experiment was described table 4. As CoCl<sub>2</sub> wt.% Increased in HCl 3N + CoCl<sub>2</sub> agent solutions, the amount of agent solution consumed for NaBH4 decomposition was increased and maximum 1.71g consumed than 3N HCl aqueous solution at HCl  $3N + CoCl_2 20$  wt.%. on the contrary, the amount of agent consumed was decreased when increasing up to CoCl<sub>2</sub> 10 wt.% in HCl 2N +  $CoCl_2$  agent solution. At this time, a maximum of 2.14 g at HCl 2N +  $CoCl_2$ 10 wt.% was consumed less than HCl 2N aqueous solution, when HCl 1N + CoCl<sub>2</sub> agent solutions. In HCl 1N + CoCl<sub>2</sub> agent solution, the amount of consumption agent solution was decreased to maximum 6.05g at CoCl<sub>2</sub> 10 wt%. The reason why consumption agent decreased at reaction pressure experiment was improved excess water by NaCl bond characteristic of CoCl<sub>2</sub> in HCl + CoCl<sub>2</sub> agent solutions. The HCl aqueous solutions has include excess water that does not participation  $NaBH_4$  decomposition. Therefore,  $CoCl_2$  was added to the excess water included in the HCl aqueous solution, it has improved to decreased agent consumption for NaBH<sub>4</sub> decomposition as shown in table 4.



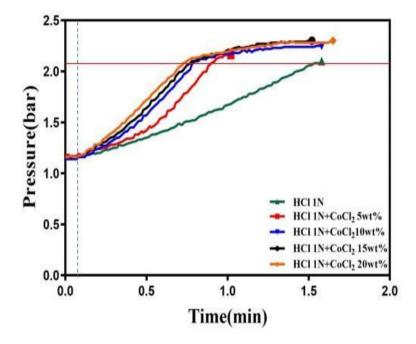


Fig. 16 Hydrogen generation pressure of HCl  $1N + CoCl_2$  agents

Table 4 Compare	spend agent	during NaBH	reaction at	each	composition agent	

CoCl <sub>2</sub> (wt.%)	Spent agent(g)				
	HC1 3N	HCl 2N	HCl 1N		
0	7.56	8.39	12.78		
5	8.91	6.53	6.73		
10	8.11	6.25	6.73		
15	8.79	6.77	7.05		
20	9.27	7.29	6.85		

# 3. Agent/NaBH<sub>4</sub> ratio and α value experiment result using agent solution

the agent solutions consumed to react with 20 g of NaBH<sub>4</sub> were measured as shown in Table 5. In Table 5, the Agent/NaBH<sub>4</sub> ratio increased when HCl normality decreased. Increasing the Agent/NaBH<sub>4</sub> ratio means that the reaction efficiency decreased. However, 3N HCl + CoCl<sub>2</sub> agent solution has decreased the Agent/NaBH<sub>4</sub> ratio maximum 1.52 times and minimum 1.03 times than 3N HCl aqueous solution. In HCl 2N aqueous solution, CoCl<sub>2</sub> addition decreased the Agent/NaBH4 ratio maximum 2.11 times and minimum 1.61 times, In HCl 1N aqueous solution decreased maximum 1.9 times and minimum 1.48 times. The maximum decreased of Agent/NaBH<sub>4</sub> reaction ratio was the HCl 3N and 2N + CoCl<sub>2</sub> 10wt%. it was increased when more than CoCl<sub>2</sub> 10 wt% in agent solutions. On the contrary, the Agent/NaBH<sub>4</sub> ratio was decreased as the amount of CoCl<sub>2</sub> increased up to 20 wt% in HCl 1N aqueous solution. However, the decrease in the Agent/NaBH<sub>4</sub> ratio does not mean that the excess water has decreased. Therefore, the excess water  $\alpha$  value at agent solutions consumed was calculated using the eq (5) as shown in Fig. 17. In HCl  $3N + CoCl_2$  agent solutions, the excess water was decreased as CoCl<sub>2</sub> increased from 5wt% to 10wt%. But, the excess water value increases from more than CoCl<sub>2</sub> 15wt%. The reason excess water increased in HCl 3N + CoCl<sub>2</sub> 15 wt% agent solutions was CoCl<sub>2</sub> decrased the amount of water that must be needed for the NaBH<sub>4</sub> decomposition. So, adding CoCl<sub>2</sub> in HCl 3N aqueous solution is not suitable for improving excess water since needed water decreased for NaBH<sub>4</sub> decomposition. On the contrary, the excess water in HCl  $2N + CoCl_2$  agent solutions was decreased as the wt% of CoCl<sub>2</sub> increases. Because the HCl 2N and have more excess water than HCl 3N. Also, the excess water in the HCl  $1N + CoCl_2$  agent solution was decreased with increasing CoCl<sub>2</sub> wt%. However, the amount of excess water in HCl 1N + CoCl<sub>2</sub> agent solutions was higher than HCl 2N +



 $CoCl_2$  agent solutions. Because the excess water in the agent solution is higher than HCl 2N + CoCl\_2 and the amount of HCl is low for NaBH<sub>4</sub> decomposition. It means that eq 6 corresponds to eq. 4 by increasing CoCl\_2 wt% in agent solutions. As a result, the excess water and Agent/NaBH<sub>4</sub> ratio can be improved with the addition of CoCl<sub>2</sub>, but it is deceased when if the amount HCl in the agent solutions low or high. Therefore, the optimal composition should be based on the HCl 2N + CoCl<sub>2</sub> decomposition agent.



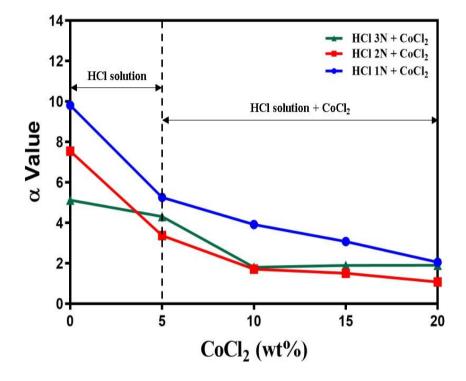


Fig. 17 Compare of excess water  $\alpha$  at each composition agent

Table 5	Agent/NaBH <sub>4</sub>	reaction	ratio	at	each	composition	agents
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CoCl <sub>2</sub> (wt.%)	Agent/NaBH <sub>4</sub> Ratio				
	HCl 3N	HC1 2N	HCl 1N		
0	4.05	5.10	5.95		
5	3.90	3.15	4.00		
10	2.65	2.41	3.6		
15	3.05	2.55	3.45		
20	3.50	2.55	3.13		



## 1) X-ray Diffraction analysis of decomposed agent solution and NaBH<sub>4</sub> reaction by-product

In the above experiment result, the reaction of NaBH<sub>4</sub> with HCl + CoCl<sub>2</sub> Agent solution decreased the excess water and Agent/NaBH<sub>4</sub> ratio. The reason for this decrease is the improvement of the excess water that does not contribute to the reaction by CoCl<sub>2</sub> at the HCl + CoCl<sub>2</sub> agent solution. The CoCl<sub>2</sub> aqueous solution has the NaCl bond characteristics after NaBH<sub>4</sub> decomposition as shown in eq (4). Therefore, rapid decomposition of NaBH<sub>4</sub> occurred at HCl of low pH, and excess water not participating in the reaction was induced to reaction using CoCl<sub>2</sub>. In this study, the agent solution and NaBH<sub>4</sub> reaction experiments are the affection of Agent /NaBH<sub>4</sub> ratio and excess water according to CoCl<sub>2</sub> wt%, which does not sufficient NaCl bond characteristics by CoCl<sub>2</sub>. In order to confirm the NaCl bond according to the addition of CoCl<sub>2</sub>, the by-products generated after the entire reaction of NaBH<sub>4</sub> 20g were analyzed using X-ray diffraction(XRD) method.

Figure 18 is a by-product sample after reaction NaBH<sub>4</sub> with agent solutions. The by-product produced after the reaction with aqueous HCl solution has white particles as shown in fig. 18. However, when  $CoCl_2$  is added in HCl aqueous solutions, the sample has black particles. The reason why produced black particles as fig.18 are due to Cobalt boride (CO<sub>2</sub>B), which is a by-product generated when the CoCl2 aqueous solution is reacted with NaBH<sub>4</sub>. [18]. Fig. 19 is a by-product XRD graph produced after reaction with NaBH<sub>4</sub> using HCl 3N aqueous solution and HCl 3N + CoCl<sub>2</sub> agent solution. In Fig. 19, NaCl peaks were clearly detected in HCl 3N aqueous solution in Fig. 20, the NaCl peak point was detected at the HCl 2N aqueous solution, but the NaCl peak point was reduced than Fig. 19. Also, the NaCl peak point at 1N HCl aqueous solution was reduced than other HCl aqueous solutions result as shown in fig 21.



The reason that decreases in NaCl peak point detection according to decreasing HCl N is the increase in excess water. Thus the entire NaBH4 reaction using HCl aqueous solution is close to eq.1, and the NaCl bond is reduced. In fig. 20, NaCl peaks point of HCl  $2N + CoCl_2$  agent solution were increased than HCl 2N aqueous solution, and complex compound combined Na, B, and H were also detected. In the case of HCl  $1N + CoCl_2$  agent solution, NaCl peak point detection increased with increasing  $CoCl_2$  wt.% same aforementioned XRD result. As a result, HCl aqueous solution has the characteristics that NaBH4 decomposes into Na, B, H due to the low pH of HCl when reacted with NaBH4, and then cations Na + and anion Cl- are combined as NaCl. However, when the HCl N is reduced, NaCl bonds decrease due to excess water increase in agent solution. Finally, the above-mentioned problem was solved by improving the excess water in which  $CoCl_2$  at agent solutions did not participate in the reaction, which affected to NaCl bond.





Fig. 18 The NaBH<sub>4</sub> by-product at each composition agent

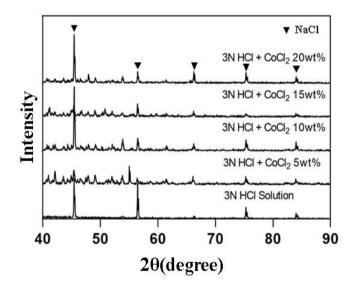


Fig. 19 X-Ray Diffraction pattern of  $NaBH_4$  after the reaction with HCl  $3N + CoCl_2$  agents



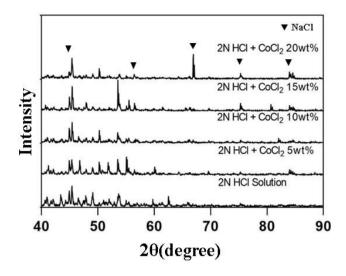


Fig. 20 X-Ray Diffraction pattern of  $NaBH_4$  after the reaction with HCl  $2N + CoCl_2$  agents

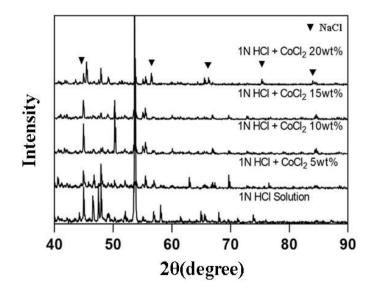


Fig. 21 X-Ray Diffraction pattern of  $NaBH_4$  after the reaction with HCl  $1N + CoCl_2$  agents



## IV. Possibility to improve energy density of fuel cell system using HCl + CoCl<sub>2</sub> agent solution

The hydrogen generation method using HCl and the solid-state NaBH<sub>4</sub> must be include water for composed an aqueous HCl solution as normality. The added water is divided into water required for the reaction and water added to composition the normality of HCl. at this time, The water to adjust the N concentration of HCl is excess water that does not contribute in the reaction. In other word, the excess water that does not contributed in the reaction has a problem of reducing energy density because unnecessary weight. Increasing the HCl normality improve excess water in HCl aqueous solution, but it has problem about hydrogen generation efficiency decreases and acid vaporization when HCl 4 normality. Therefore, this study focused the characteristics of NaBH4 and HCl reaction because increasing the HCl N does not suitable improvement excess water. NaBH4 has the characteristics of NaCl bond after accelerated reaction with HCl. On the contrary, water that does not contribute in the reaction is reacted as in eq. (1). However, the eq. (1) is a theoretical reaction and does not consider room condition, it means reduced the hydrogen generation efficiency. Therefore, CoCl<sub>2</sub> was added at HCl aqueous solution to improve the excess water that does not participating in the reaction using NaCl bond. The CoCl<sub>2</sub> has the NaCl bond characteristic when reacting with NaBH4 as in eq. (4). Decomposition of NaBH4 using the above-mentioned HCl and CoCl<sub>2</sub> NaCl bond reduced excess water and Agent/NaBH<sub>4</sub> ratio than HCl aqueous solution. In addition, XRD analysis showed that NaCl peak point detection decreases when the HCl N decreases, and NaCl peak point detection increases when CoCl<sub>2</sub> is added. As a result, the NaBH<sub>4</sub> that decomposed at below HCl 2N does not sufficiently NaCl bond, but CoCl<sub>2</sub> in agent solution affected NaBH4 decomposition as NaCl bond. Based on the experimental results, the HCl + CoCl<sub>2</sub> agent solution decreased the amount of



agent consumed for NaBH<sub>4</sub> decomposition than the HCl aqueous solution, also it suitable solve the problem of reaction efficiency when decreasing the HCl N concentration. Therefore, the HCl +  $CoCl_2$  agent solution promises the improve the energy density of the fuel cell system that using the solid-state NaBH<sub>4</sub> as hydrogen storage and supply.



### Conclusion

In this study, the HCl+CoCl<sub>2</sub> agent solution was proposed to decompose the solid-state NaBH<sub>4</sub> and improve the energy density of fuel cell unmanned aerial vehicles. The hydrogen generation method at solid-state NaBH<sub>4</sub> is NaBH<sub>4</sub> aqueous solution and using catalyst. However, the NaBH<sub>4</sub> aqueous solution has a serious problem that unstable long-term storage and low yield rate. In addition, NaOH is must be added to maintaining NaBH<sub>4</sub> aqueous solution, and it does not participate in the reaction. It means a decrease in hydrogen storage density and energy density. In order to solve the aforementioned problems, Recently, direct hydrogen generation methods using solid-state NaBH<sub>4</sub> have been studied in order to solve the aforementioned problems. The NaBH4 exists in the solid-sate at room condition so it is promised long-term storage. also, the aforementioned catalytic problem is improved using a hydrochloric acid solution that solid-state NaBH<sub>4</sub> agent solution. The use of HCl as an agent solution has the advantage of accelerated NaBH<sub>4</sub> decomposition, but there is a problem of corrosion caused by low pH and a decrease in hydrogen generation efficiency due to a decrease in HCl N. Also, the water for the composition of the HCl N is consists of water that participates for the reaction and excess water that does not contribute to the reaction. The excess water that does not contribute to the reaction has a problem of reducing the energy density. To solve this problem, the CoCl<sub>2</sub> was selected for the improvement of excess water in HCl aqueous solutions. The hydrogen decomposed in NaBH4 was measured using an MFM to confirm the hydrogen decomposition characteristics when the HCl and CoCl<sub>2</sub> aqueous solution reacted with solid-state NaBH<sub>4</sub>. The HCl aqueous solution has a characteristic that accelerated NaBH<sub>4</sub> decomposition to generated hydrogen. On the contrary, when solid-state NaBH<sub>4</sub> decomposed using CoCl<sub>2</sub> aqueous solution, the decomposition was started when after 143 seconds at CoCl<sub>2</sub> 5wt.% aqueous solution and hydrogen was gradually generated.

When CoCl<sub>2</sub> increased to 10 wt.%, The reaction start time was reduced, but the experimental data does not reliable result by exceeded the maximum flow measurement of MFM equipment. rate Therefore, the experiment was re-configuration to solve the problems that experiment methods of using MFM device. The re-configuration experimental method was as follows. First, the reactor of the sealing structure was used without using the existing MFM device and second, the experiment was configurated that measuring the consumed time when the hydrogen generated by the NaBH<sub>4</sub> decomposition in the reactor reached the set pressure 2.1 bar. The agent solution for solid-state NaBH<sub>4</sub> decomposition was composed what combinated HCl 1N, 2N, 3N, and CoCl<sub>2</sub> 5wt.% 10wt.%, 15wt,% 20wt,%. In the HCl aqueous solution, the consumption time that reached the set pressure when decreased the HCl N was more consumed 1.7 times at HCl 1N more than HCl 3N. In the HCl + CoCl<sub>2</sub> agent solution, the HCl 3N + CoCl<sub>2</sub> composition has not sufficiently affected to NaBH<sub>4</sub> decomposition. However, the consumed time at reached the set pressure using HCl  $2N + CoCl_2$ agent solution was the average 0.78 minutes less than the HCl 2N aqueous solution. also, the consumed time that reached set pressure using HCl 1N + CoCl<sub>2</sub> agent solution was average 0.81 minutes less than the HCl 1N aqueous solution. In addition, the Agent/NaBH<sub>4</sub> ratio decreased by a maximum of 2.11 times in HCl 2N + CoCl<sub>2</sub> 10wt.% and the excess water that did not contribute in the reaction decreased by 7.82 moles in the HCl 1N + CoCl<sub>2</sub> 20wt.%. Finally, the NaBH<sub>4</sub> by-product that produces in the above experiment was analyzed using XRD analysis method. In the XRD analysis, the NaCl peak point decreased as the normality of HCl aqueous solution decreased. also, the peak that by-product of combined Na, B, and H was detected as the NaCl peak was decreased. on the contrary, the NaCl peak was increased in HCl 2N, 1N + CoCl<sub>2</sub> agent solutions. Because the NaBH<sub>4</sub> that decomposed at low HCl N concentration was affected by NaCl bond of CoCl<sub>2</sub> in agent solutions.



Based on the experimental results, the agent solution that combined  $CoCl_2$  and HCl aqueous solution are improved the Agent/NaBH<sub>4</sub> rato than HCl aqueous solution and the excess water that does not contribute to reaction reduced. Increasing the Agent/NaBH<sub>4</sub> ratio and the decreasing excess water was promised improvement the weight of the fuel cell system that using solid-state NaBH<sub>4</sub> as hydrogen storage and source, it means that improved the limited energy density of the fuel cell system. In other words, the increasing flight time of a UAV using a fuel cell as a power source was promised.



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#### 감사의 글

이 논문은 공부하는 것을 어려워하며 등지고 살아온 한 학생이 부족한 것 을 느끼고 배우며 어려워하는 것에 도전하는 방법을 배운 대학원 과정 중에 서의 작은 결실입니다.

어느새 2년의 석사 학위 과정을 마치고 학위논문을 제출하게 되었습니다. 학부 2학년부터 석사 2년까지 총 5년간의 시간 동안 작은 결실을 이루도록 저에게 도움을 주신 많은 분이 있습니다. 부족하지만 학위 논문을 마치면서 그분들께 감사의 말씀을 전합니다.

항상 진심 어린 조언을 해주시며, 석사 학위를 마치는데 그 누구보다 많은 도움을 주시고 학생의 의견을 항상 존중해주신 김태규 지도교수님께 진심으 로 감사드립니다.

또한 김태규 지도교수님에게는 항상 죄송한 마음이 앞서서 글로 작성하여 진심을 담기에는 부족하지만, 김태규 지도교수님 학생으로 5년 동안 연구한 날 중 후회 없이 항상 즐거운 마음으로 보내게 되어 다시 한 번 감사의 말 씀을 전합니다. 이 학위 논문을 작성하는 동안 관심어린 지도를 해주신 이현 재 교수님과 이창열 교수님께도 진심어린 감사의 마음을 전합니다.

이 연구를 진행하는데 아낌없이 물심양면으로 지원해주신 휴그린파워(주) 강신왕 대표님께도 진심어린 감사의 마음을 전합니다.

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바쁘다는 이유로 연락을 자주 하지 못했지만, 대학교에 입학할 수 있도록 군 전역 후 공부하는 법과 공부를 해야 하는 이유를 가르쳐준 또 다른 스승 인 백승철에게 진심어린 감사의 마음을 전합니다.

마지막으로 어느 날 가족들에게 찾아가 공부하고 싶다고 말했을 때 의심 없이 믿어주시고, 힘들 때 부모로서 또는 인생의 선배로서 아낌없는 지원과 조언을 해주신 어머님 아버님 감사하고 사랑합니다.