

DEVELOPMENT OF SOLID SODIUM BOROHYDRIDE HYDROGEN GAS
GENERATOR FOR PORTABLE PEM FUEL CELL APPLICATIONS

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GAS GENERATOR FOR PORTABLE PEM FUEL CELL APPLICATIONS**

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ABSTRACT

DEVELOPMENT OF SOLID SODIUM BOROHYDRIDE HYDROGEN GAS GENERATOR FOR PORTABLE PEM FUEL CELL APPLICATIONS

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Hydrogen is considered as a promising candidate to replace fossil fuels. For implementing a hydrogen based infrastructure, hydrogen storage is the main obstacle that is needed to be overcome. Being boron based compound, sodium borohydride, NaBH_4 , is a convenient hydrogen storage material for applications like unmanned air vehicles. There are several issues behind commercialization of NaBH_4 hydrolysis systems. This doctorate thesis aims to be solution of NaBH_4 hydrolysis system by highlighting three main contributions. First, the usage of solid state NaBH_4 enables to increase the gravimetric H_2 storage capacity of the system in order to meet international targets. Second, solid NaBH_4 usage decreases the system's weight since it does not require a separate fuel storage tank, which is very important for practical applications. Finally, by using accessible and effective catalysts like FeCl_3 and CoCl_2 it decreases the system's cost. In this study catalyst was added by following two methodologies. In the Case 1, solid catalyst was placed in a glass reactor with solid NaBH_4 and water added to initiate the hydrolysis reaction. The water amount is found to be a critical parameter that should be optimized. The maximum hydrogen generation rate was obtained for Case 1 is 1.88L/min with an efficiency of 63.5% when 5g of NaBH_4 , 0.5 g FeCl_3 and 33.3g water was used. In Case 2, solid NaBH_4 was placed in a glass reactor. Solid catalyst was dissolved in desired amount of water to obtain catalyst solution. This catalyst solution was added into the reactor to generate hydrogen. The

maximum hydrogen generation rate was obtained for Case 2 is 2.6L/min when 10g NaBH₄, 1g FeCl₃ was dissolved in 66.6g water with an efficiency of 76.28%. This condition is used in the integrated developed solid NaBH₄ system with PEMFC. This is the first time that solid state sodium borohydride hydrolysis system was tested for PEM fuel cell performance.

Keywords: Solid sodium borohydride, Energy, PEM Fuel Cell, Hydrogen, Portable applications

ÖZ

TAŞINABİLİR PEM YAKIT PİLİ UYGULAMALARI İÇİN KATI SODYUM BORHİDRÜR HİDROJEN GAZ JENERATÖRÜNÜN GELİŞTİRİLMESİ

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Hidrojen fosil yakıtlara alternatif olarak gösterilen en önemli enerji kaynağıdır. Hidrojene dayalı bir ekonomi sistemine doğru geçişte en büyük engel olarak hidrojen depolama sorunu görülmektedir. Bor bazlı bir bileşik olan sodyum borhidrür, NaBH_4 , insansız hava araçları gibi uygulamalara yönelik daha uygun bir hidrojen depolama yöntemidir. Ancak NaBH_4 hidrolizinden hidrojen elde yönetiminin de yaygınlaştırılmasında bazı sorunlar vardır. Bu doktora tezi sodyum borhidrür hidrolizinin ticarileştirilmesindeki önemli üç etkene vurgu yaparak çözüm sağlamayı hedeflemektedir. Bunlardan ilki, katı fazda NaBH_4 kullanarak sistemin ağırlıksal olarak hidrojen depolama kapasitesini evrensel hedeflerini karşılayacak şekilde arttırmaktadır. İkinci olarak, katı fazda sodyum borhidrür kullanarak ayrı bir sodyum borhidrür solüsyonu için gereken depolama tankına gereksinimi ortadan kaldırdığı için sistemin ağırlığını azaltmaktadır. Sistem ağırlığı taşınabilir uygulamalar için önemli bir parametredir. Son olarak ise ucuz, etkili ve yaygın olarak bulunabilen FeCl_3 ve CoCl_2 gibi katalizör kullanarak sistem maliyetini düşürmektedir. Bu çalışmada katalizör reaktöre 2 farklı yöntem kullanılarak eklenmektedir. Yöntem 1’de, katı katalizör ve katı NaBH_4 , camdan yapılan rekatör içerisine yerleştirilir ve üzerine su eklenerek H_2 üretimi başlatılır. Eklenen su miktarının optimize edilmesi gereken en önemli parametre olduğu bulunmuştur. Yöntem 1 için elde edilen en yüksek H_2 üretim hızı 1.88L/dk ve

verimi ise % 63.5 olarak bulunmuştur. Bu durumda 5g NaBH₄, 0.5 g FeCl₃ ve 33.3g su kullanılmıştır. Yöntem 2'de ise, sadece katı NaBH₄ reaktör içerisine yerleştirilir. Katı katalizör istenilen miktar su içerisinde çözülerek katalizör çözeltisi elde edilir. Bu katalizör çözeltisi H₂ üretimini başlatmak için reaktöre eklenir. Yöntem 2'de elde edilen en yüksek H₂ üretim hızı 2.6L/dk olup 10g NaBH₄, 66.6g su içerisinde 1g FeCl₃ çözülülerek kullanılmıştır. Verim ise %76.28 olarak hesaplanmıştır. Bu Yöntem 2'de elde edilen durum geliştirilen NaBH₄ sisteminin yakıt pili ile entegrasyonu için kullanılmıştır. Bu tez katı fazda NaBH₄ hidrolizinin PEM yakıt pili performansında test edilmesinin ilk örneğidir. Ayrıca, geliştirilen bu sistemin taşınabilir uygulamalar için PEM yakıt piline gerekli hidrojeni sağlayabilecek kapasitede olması hedeflenmektedir.

Anahtar Sözcükler: Katı Sodyum Borhidrür, Enerji, Hidrojen, PEM yakıt pili, Taşınabilir Uygulamalar

To Murat, Şenay and Defne.

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LIST OF SYMBOLS AND ABBREVIATIONS

V_{H_2} = Volume of Hydrogen(L)

V_{theo,H_2} = Volume of Theoretical Hydrogen(L)

P: Pressure

T: Temperature

PEMFC: Proton Exchange Membrane Fuel Cell

DBFC: Direct Sodium Borohydride Fuel Cells

B-PEMFC: Proton exchange membrane fuel cell uses sodium borohydride as fuel

N_{H_2} = Moles of Hydrogen(mol)

N_{NaBH_4} = Moles of sodiumborohydride(mol)

x="hydration factor"

MWt = Molecular weight (g / mol)

GHSC: Gravimetric Hydrogen Storage Capacity

HGR: Hydrogen Generation Rate

W_{el} = the electrical work in units of J/mol

q= charge (Coulombs/mol)

E=Potential of fuel cell in units of Volts.

n=number of electrons per molecule of H₂ that is 2 electrons per molecule.

N_{Avg} =number of molecules per mole that is Avogadro's number= 6.022×10^{23}
molecules/mol

q_{el} =charge of one electron= 1.602×10^{-19} Coulombs/electron

F =Faraday's constant (F) with the value of 96485 Coulombs/electron.mol

η =Efficiency of the fuel cell

W_{H_2} =energy value of hydrogen consumed (J/s=W)

ΔG =Gibbs free energy (J/mol)

ΔH =hydrogen's higher heating value =286kJ/mol

CHAPTER 1

INTRODUCTION

There is no doubt that world needs a renewable, sustainable energy source to maintain the existence of human kind. Today's economy based on fossil fuels may replace itself by named "hydrogen based economy" due to the depletion of fossil fuel reserves and negative impact on nature.

Hydrogen being a most abundant element in universe is not found in its molecular form. Thus, it should be synthesized from other sources. Hydrogen sources to be considered must be renewables in order not to damage world's natural balance. Table 1 shows the comparison of heat energy produced by combustion of some selected fuels.

Table 1 Combustion energy of some common fuels [1]

| Fuel | Heat Energy of Combustion (kJ/g) |
|-------------|---|
| Petroleum | 43.10 |
| Paraffin | 43.10 |
| Graphite | 32.64 |
| Castor oil | 39.33 |
| Wood | 17.57 |
| Hydrogen | 142.26 |

As can be seen from Table 1, hydrogen has highest heat energy of combustion. Besides from combustion, hydrogen is lightest, most efficient and cleanest fuel. Moreover, it can be used directly in fuel cells in order to obtain electricity. So, it is a promising clean energy source in order to replace fossil fuels.

There are several technical barriers in front of the hydrogen infrastructure that must be addressed before commercialization. One of the most crucial obstacles behind hydrogen economy is the hydrogen storage. The hydrogen storage systems found in literature or in market are heavy and huge so they are not suitable for the portable applications of fuel cells. Developing safe, reliable, compact and cost effective hydrogen storage systems is crucial for fully understanding of the potential of energy system based on hydrogen as an energy carrier and to compete with currently existing technologies. Being boron based compound, sodium borohydride, NaBH_4 , is a convenient hydrogen storage material for applications like unmanned air vehicles. It is evident that, the world progresses towards the hydrogen infrastructure. Therefore, the usage of NaBH_4 for hydrogen storage will increase the boron consumption which results an increase of the value of the boron resources in TURKEY as an energy carrier. Furthermore, sodium borohydride is an efficient source which releases hydrogen gas in the amount double of its hydrogen content upon hydrolysis in water. The hydrolysis reaction is a rapid, irreversible, heterogeneous and exothermic reaction.

The present thesis will focus on hydrolysis of solid NaBH_4 for hydrogen generation.

The objectives of this doctorate study are;

- i. To develop a hydrogen storage system based on solid NaBH_4 for supplying on demand and continuous hydrogen for proton exchange membrane (PEM) fuel cell for electricity production for portable applications.
- ii. This system will use solid NaBH_4 instead of using stabilized NaBH_4 aqueous solution for decrements in the system's weight by using limited

amount of water. Also, using solid system simplifies the refueling strategy of the fresh fuel into the system.

- iii. In the aqueous systems although stabilizer is added to the solution, self hydrolysis of NaBH_4 cannot be suppressed for long period of time. Therefore, it is aimed to increase the shelf life of storage system by implementing solid NaBH_4 storage.
- iv. To perform hydrolysis reaction experiments on effective and accessible non-noble metal catalysts like FeCl_3 and CoCl_2 in order to decrease the system's cost.
- v. To perform hydrolysis reaction experiments in a semi-batch reactor with different reactor sizes in order to understand the effect of reactor geometry.
- vi. To integrate the sodium borohydride reactor to Proton Exchange Membrane fuel cell (PEMFC) in order to meet its continuous hydrogen requirement.
- vii. This will be the first time that solid NaBH_4 system tested for PEMFC performance.

In the following chapter; (Chapter 2) detailed literature survey about hydrogen storage methods, sodium borohydride properties, fuel cell types for integration of sodium borohydride system and catalyst research of hydrolysis of sodium borohydride are explained comprehensively with recent literature studies.

In Chapter 3; chemistry of hydrolysis reaction is given. In Chapter 4, methodologies and scope of kinetic experiments are mentioned in detail. The experimental results are given in Chapter 5. Chapter 6 covers the integration of sodium borohydride prototype system with fuel cell operation.

As a final chapter, conclusions and further recommendations are stated in Chapter 7. The thesis is completed with references and appendices sections that provide additional data.

CHAPTER 2

LITERATURE REVIEW

Hydrogen is clean, highly abundant and non-toxic renewable. It releases only water vapor when it burns. However, it is not found in its molecular form. It must be produced from other renewable sources in order to eliminate the greenhouse gas emissions.

Hydrogen storage is one of the most challenging issues behind “hydrogen economy”. Hydrogen can be stored as compressed gas, liquefied hydrogen, in a chemical compound (i.e. metal and chemical hydrides), or physically stored in porous structures. A major consideration for these storage methods in terms of hydrogen efficiency is the cost of energy required to get hydrogen in and out of the storage system [2]. Figure 1 shows the classification of hydrogen storage methods.

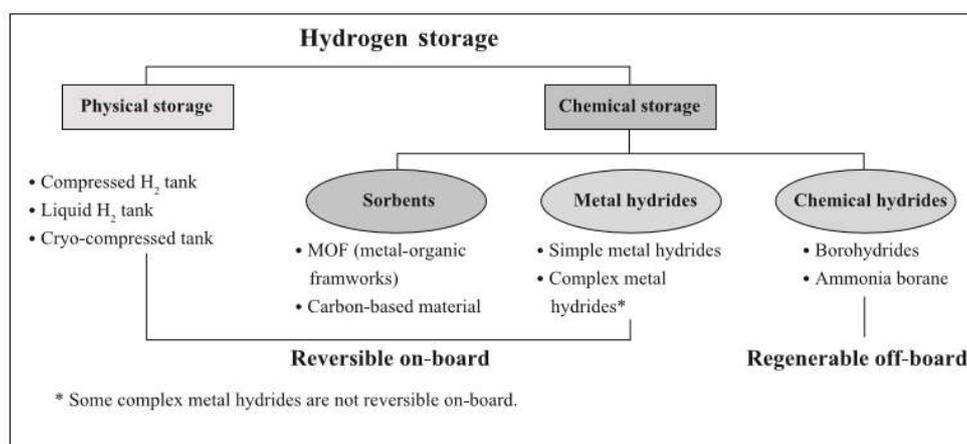


Figure 1 Hydrogen Storage Methods [1]

Each hydrogen storage method incorporates its own advantageous and disadvantages. This thesis concentrates on sodium borohydride (NaBH_4) as a chemical hydride for hydrogen supply for proton exchange membrane fuel cells (PEMFC).

2.1 Properties of Sodium Borohydride

Sodium borohydride is a well-known chemical which is abundantly used as a reducing agent in pharmaceutical industry. For better understanding the hydrolysis of sodium borohydride to generate hydrogen, its physical and thermodynamic properties are listed in Table 2 and Table 3.

Table 2 Physical Properties of Sodium Borohydride [11]

| | |
|------------------------------|--|
| Molecular Weight | 37.84 g/mol |
| Colour | White |
| Crystalline form (anhydrous) | Face centered cubic $a= 6.15\text{\AA}$ |
| Melting Point | 505°C (10 bar H_2) Decomposes above 400° C in vacuum |
| Thermal Stability | It will not ignite above 400°C on a hot plate Ignites from free flame in air, Burning quietly |
| Density | 1.074 g/cm ³ |

Table 3 Thermodynamic properties of Sodium Borohydride [11]

| Sodium Borohydride (NaBH₄) | |
|--|-----------------|
| Free energy of formation | - 125.82 kJ/mol |
| Heat of formation | - 190.32 kJ/mol |
| Entropy | 101.41 J/mol.K |
| Heat capacity | 86.40 J/mol.K |
| Free energy of ionization NaBH ₄ (s)=Na ⁺ +BH ₄ ⁻ | - 23.66 kJ/mol |
| Borohydride ion, BH₄⁻ | |
| Free energy of formation | - 119.55 kJ/mol |
| Heat of Formation | 51.83 kJ/mol |
| Entropy | 106.59 J/mol.K |
| Heat of hydrolysis $BH_4^- + H^+ + 3H_2O(liq) \rightarrow H_3BO_3 + 4H_2(g)$ | -371.18 kJ/mol |
| Half electric reaction $BH_4^- + 8OH^- \rightarrow B(OH)_4^- + 4H_2O + 8e^-$ | 1.24V |

The most important physical property of NaBH₄ for hydrolysis reaction is solubility in water. Solubility of NaBH₄ and NaBO₂ in water were investigated by Kojima et al. [12]. They found the temperature dependence of the water solubility of NaBH₄ and NaBO₂ as in Equation 2.1 and Equation 2.2 respectively:

$$\text{Solubility of NaBH}_4 = -261 + 1.05 \times T(K) \text{ g/100gwater} \quad (2.1)$$

$$\text{Solubility of NaBO}_2 = -245 + 0.915 \times T(K) \text{ g/100gwater} \quad (2.2)$$

Sodium borohydride's potential of hydrogen source was first investigated by Schlesinger et al. (1953) [4] and over 60 years, the hydrolysis of sodium borohydride had been investigated for overcoming the drawbacks and commercialization yield as a hydrogen production method.

NaBH₄ has high gravimetric hydrogen storage capacity of 10.8wt% and yield high purity of hydrogen. The reaction is controllable. Byproduct of this reaction is water soluble sodium metaborate (NaBO₂) which is nontoxic and environmentally safe. [5] Figure 2 shows the hydrogen cycle with NaBH₄.

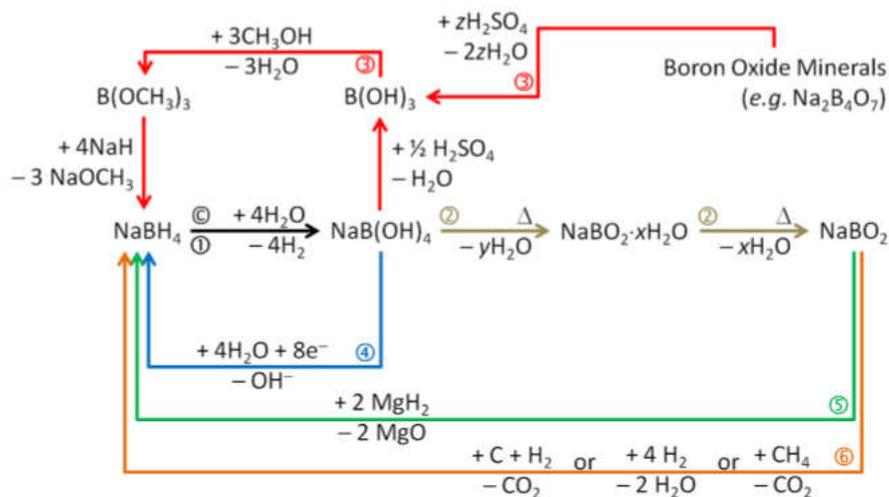
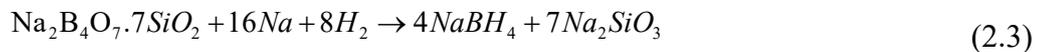


Figure 2 Hydrogen cycle with sodium borohydride [7]

In Figure 2, symbol © denotes catalyst in the catalytic hydrolysis reaction. With ②, the thermal dehydration of sodium tetrahydroxyborate NaB(OH)₄ is shown. ③ denotes the BrownSchlesinger process. ④ is the electrochemical process. ⑤ denotes the modified Bayer process and finally, ⑥ denotes the reduction process with three different reducing agents.

There are more than 100 methods available in literature for production of NaBH₄. Among them Brown Schlesinger process and Bayer process is promising due to its practical application method. The Schlesinger method is an organic process in which sodium hydride is prepared in a mineral oil medium at about 275 °C in a reactor then transferred to another reactor where trimethyl borate is added to react with sodium hydride to produce sodium borohydride. After this reaction, a complex separation procedure including crystallization and drying is applied in order to recover pure sodium borohydride. Overall yield of this process is over 90%. [11]

On the other hand, Bayer process is an inorganic process for manufacturing NaBH₄. In the Bayer's process, borosilicate (Na₂B₄O₇·7SiO₂) is produced by fusion from borax (Na₂B₄O₇) and quartz sand (SiO₂). Then, the borosilicate is cooled, ground and reacted with sodium in the presence of hydrogen at 300kPa and elevated temperatures of 400-500 °C. The produced sodium borohydride is extracted from the solution with liquid ammonia under pressure which yields over 90%. The reaction of Bayer's process is shown in Equation 2.3. [11]



2.2 Sodium Borohydride as a Fuel for Fuel Cells

The use of sodium borohydride in fuel cells can be divided into two main systems: Direct Sodium Borohydride Fuel Cells which directly uses aqueous sodium borohydride solution at the anode (DBFC) and Proton Exchange Membrane Fuel Cells which uses on site generated H₂ from hydrolysis of sodium borohydride (B-PEMFC). Each system has its own advantages and disadvantages. [3]

The main advantage of using DBFC system is its high theoretical energy density which is 9.3 Wh/g NaBH₄ and there is no fuel processor needed by using solution as fuel. Moreover, for electrocatalysts, other than platinum, cheap and non-noble metal alternatives are available. On the other hand, there are remaining challenges for DBFC. The development of effective anode catalysts is needed to generate

electrons for reduction of BH_4^- ion as well as inhibiting the H_2 generation. Also, the developed catalysts should be tolerant to deactivation. Furthermore, treatment of NaOH accumulation at both cathode and anode is critical for fuel cell system. [3] Figure 3 shows the picture of DBFC.

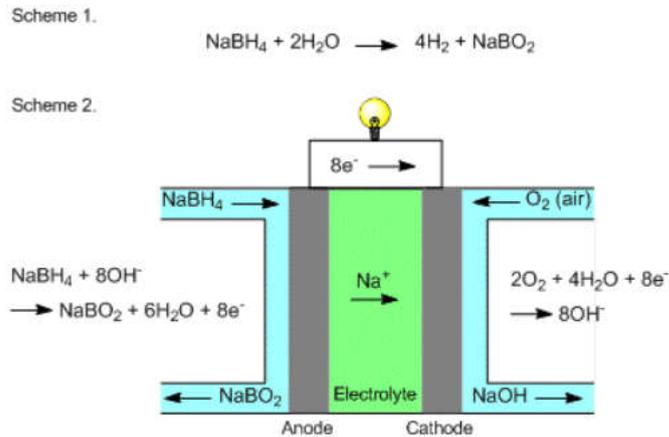


Figure 3 Picture of DBFC [83]

For B-PEMFC systems, the main advantage of H_2 generation is being on site so, it can be controlled independently. There are many electrocatalysts alternatives available in literature for anode side of PEMFC. NaBH_4 can be quickly refueled simply by filling the reservoir with fresh NaBH_4 solution. Hydrolysis of NaBH_4 presents water vapor in the system so this water vapor can be used to humidify the PEMFC membranes. Moreover, water generated by PEMFC can be recycled to the NaBH_4 solution allowing additional H_2 to be generated. On the other hand, for remaining issues in B-PEMFC systems: the optimum catalyst selection and its amount is critical for development of an economic hydrolysis reaction of NaBH_4 with high conversion and optimum reaction rate. The selected catalyst should be tolerant to deactivation. As well as design of the hydrolysis reactor which is suitable for on-site generation of H_2 is necessary. The product should be treated in order not to block the active sites of the catalyst. Simple refueling system for fresh NaBH_4 solution is needed. Moreover, water re-using system between PEMFC and hydrolysis reactor should be cared carefully for weight of the system. Finally, a compact design of NaBH_4 reactor is needed for interconnection to PEMFC for establishment of an effective system. [3]

Figure 4 shows the schematic diagram for B-PEMFCs.

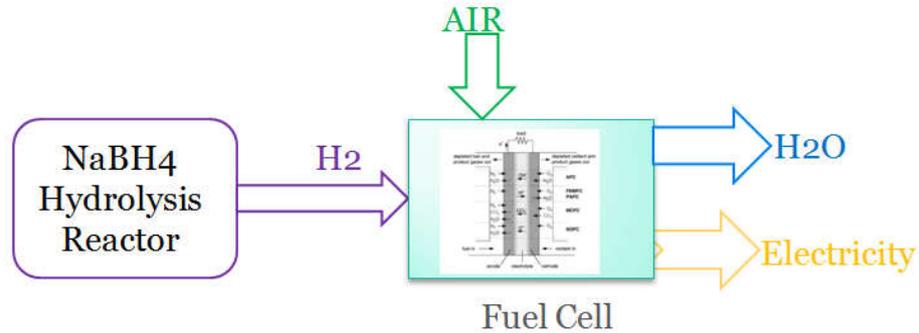
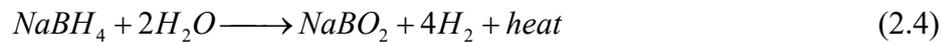


Figure 4 Schematic diagram for B-PEMFCs

This thesis aims to develop a sodium borohydride hydrolysis system for B-PEMFCs for portable applications.

2.3 Catalytic Hydrolysis of Sodium Borohydride

The chemistry of the hydrolysis reaction will be discussed in detail in the Chapter 3. The stoichiometric hydrolysis reaction can be written as follows:



The reaction is highly exothermic with a heat of reaction of -217kJ/mol. The reaction rate is strongly dependent on initial NaBH₄ concentration. This reaction can occur without catalyst that is called self-hydrolysis of sodium borohydride. But, the productivity of hydrogen from self-hydrolysis of NaBH₄ at room temperature is very low due to increase of pH during the hydrolysis reaction. This increase of pH results from the formation of strongly basic sodium metaborate ion as by-product. [6] So, catalyst is needed for higher hydrogen production productivity. In literature, many researches had been done to synthesize the effective catalyst in order to accelerate hydrolysis reaction. The catalysts which can be used for hydrolysis reaction can be categorized as non-noble metal catalysts, transition metal salts and noble metal catalysts.

In the following Sections 2.3.1, 2.3.2 and 2.3.3, detailed literature review was done related to the catalyst nature.

2.3.1 Non-noble Metal Catalysts

Non-noble metal catalysts were promising in terms of cost of catalyst.

In Table 4, researches done by using various non-noble metal catalysts was reported in order of year. The maximum H₂ generation rates were reported with the experiment conditions including concentrations of NaBH₄ and NaOH as well as the reactor temperature. Also, the preparation methods of selected catalysts were given.

Table 4 Literature Review on Non-Noble Metal Catalysts

| Year, Ref | Catalyst | Form/ Preparation Method | Max H ₂ generation rate (L H ₂ /min/g) | NaBH ₄ Conc. (wt%) | NaOH Conc. (wt%) | Temp. (°C) |
|---------------|-----------------------------------|--------------------------------|---|-------------------------------------|------------------------|---------------|
| 2001, [13] | Fluorinated Mg ₂ Ni | Powder | 0.58 | -- | 10 | 25 |
| 2003, [14] | Ni _x B | Powder | 0.15 | 1.5 | 10 | 20 |
| 2004, [15] | Filamentary Ni-Co | Doctor blading | 0.1 | 10 | 0.4 | 25 |
| 2005, [16] | Co-B | Powder | 2.97 | 2 | 5 | 15 |
| 2007, [17] | Co-P/Cu | Electroplating | 0.95 | 10 | 1 | 30 |
| 2007, [18] | Co-B/Ni foam | Dip-coated | 7.20 | 25 | 3 | 20 |
| 2007, [19] | Co-Mn- B/Ni foam | Electroplating | 1.20 | 5 | 5 | 20 |
| 2007, [20] | Co-B | Powder | 2.40 | 20 | 5 | 20 |
| 2007, [20] | Ni-Co-B | Powder | 2.61 | 2.7 | 15 | 28 |

Table 4 (cont'd) Literature Review on Non-Noble Metal Catalysts

| | | | | | | |
|---------------|------------------------------------|---------------------------------|------|-----|----|----|
| 2008, [22] | Co-B/Glass | Thin film prepared by PLD | 5.02 | 0.1 | 4 | 25 |
| 2008, [23] | Co/PPX-Cl | Metallised films | 4.25 | 2.5 | 10 | 25 |
| 2008, [24] | Co-B/Pd | Dry dip coated | 2.88 | 20 | 4 | 30 |
| 2008, [25] | Co-W-B/Ni foam | Electroless plating | 15.0 | 20 | 5 | 30 |
| 2008, [26] | Co-B (from LiCoO ₂) | Powder | 2.4 | 0.5 | -- | 40 |
| 2008, [27] | Ni-B-Si | Powder | 1.92 | 0.6 | -- | 25 |
| 2008, [28] | Ni(0) nanoclusters | Stabilised on PVP | 4.25 | 0.6 | 0 | 25 |
| 2008, [29] | Co- B/MWCNTs | Powder | 5.1 | 20 | 3 | 30 |
| 2008, [30] | Co-B NPs | Powder | 26 | 15 | 5 | 30 |

Table 4 (cont'd) Literature Review on Non-Noble Metal Catalysts

| | | | | | | |
|---------------|---------------------------------|---------------------------------|------|-----|-----|----|
| 2009, [31] | C-P-B | Powder | 2.12 | 1 | 1 | 25 |
| 2009, [32] | Co-Ni-P/Cu | Electroplating | 2.48 | 10 | 10 | 30 |
| 2009, [33] | Co(0) nanoclusters | Intrazeolite | 6.08 | 0.6 | 10 | 25 |
| 2010, [34] | Fe-Co-B/Ni foam | Electroless plating | 22 | 15 | 5 | 30 |
| 2010, [35] | Co-Ni-B | Powder | 1.18 | 1 | 1 | 25 |
| 2010, [35] | Co-Mo-B | Powder | 2.88 | 1 | 1 | 25 |
| 2010, [36] | Co-P | Electroless plating | 1.85 | 5 | 1 | 30 |
| 2010, [37] | Co-P- B/Glass | Thin film prepared by PLD | 4.23 | 0.1 | 0.4 | 25 |
| 2011, [38] | Co-Ni-P/Pd- TiO ₂ | Electroless plating | 0.46 | 1 | 10 | 25 |
| 2011, [39] | Co/SiO ₂ | Wetness impregnation | 2.51 | 5 | 5 | 40 |

Table 4 (cont'd) Literature Review on Non-Noble Metal Catalysts

| | | | | | | |
|---------------|--|-------------------------|-------|-----|----|----|
| 2011, [40] | Ni-Co-B | Powder | 0.71 | 5 | 10 | 20 |
| 2012, [41] | Co/ZIF-9 | Solvothermal method | 2.35 | 0.5 | 5 | 30 |
| 2012, [42] | Co-B/TiO ₂ | Wetness impregnation | 12.50 | 1 | 4 | 30 |
| 2012, [43] | Co/CCS | Wetness impregnation | 10.40 | 1 | 10 | 20 |
| 2012, [44] | Co-P/Ni foam | Electroless plating | 0.93 | 15 | 5 | 25 |
| 2013, [50] | Co-Mo-B | Chemical reduction | 19 | 5 | 5 | 30 |
| 2014, [49] | (Ni-Co-P/ γ - Al ₂ O ₃) | Electroless plating | 6.60 | 2 | 10 | 55 |
| 2015, [48] | bimetallic Ni-Co nanoparticle | Electroless plating | 1.28 | 10 | 5 | 40 |

Table 4 (cont'd) Literature Review on Non-Noble Metal Catalysts

| | | | | | | |
|---------------|---|------------------------|-------|----|----|----|
| 2016, [45] | Co-Sn- B/GP | in situ reduction | 11.27 | 5 | 5 | 30 |
| 2016, [46] | Ni-B | Electroless plating | 4.99 | 5 | 1 | 30 |
| 2017, [47] | porous Co ₂ P nanowires (NWs) | hydrothermal method | 4.03 | 10 | 10 | 30 |

As can be seen from Table 4, there are many non-nobel metal catalysts available in literature. Each research focuses on different point. So, the NaBH₄, NaOH concentrations vary as well as reactor temperature, resulting that comparison between different catalyst cannot be done comprehensively.

In order to interpret the reaction rate variations with respect to catalyst type and nature, the hydrolysis reaction mechanism should be understood effectively. Holbrook and Twist (1971) [10] were the first to postulate a working mechanism for reaction kinetics in heavy water (D₂O). This mechanism is still most widely accepted mechanism proposed on the catalytic hydrolysis of NaBH₄ for both noble and non-noble catalysts. Figure 5 shows this mechanism where M denotes metal active site and e_M denotes electron transferred from the BH₄⁻ ion to the metallic surface. Then it reduces a proton taken from the adsorbed water.

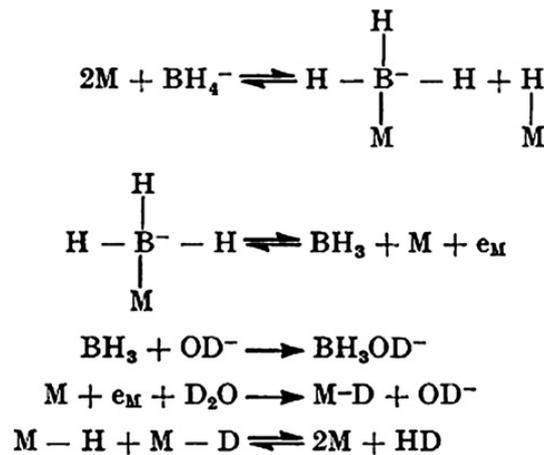


Figure 5 Reaction mechanism for aqueous NaBH₄ [10]

The rate determining step was found to be the breaking of the O-H bond of water for reducing the proton. This step produces partially hydrolyzed BH₃(OH)⁻ ion which then hydrolysis to complete the reaction to the end product of hydrated metaborate ion.

As can be seen from Table 4, the most common catalyst material that has been investigated was Co-B alloy. The reason why Co-B is used instead of metallic Co is the fact that without boron, metallic cobalt shows minimal activity. This issue is explained by boron is believed to act as an electron donor to the active sites of Co. This idea is supported by XPS analysis of Co-B which shows a positive shift in

binding energy of boron compared to its elementary form. The addition of boron improves the electron transfer from active metal sites to the absorbed water molecules at the rate determining step which is explained above in Holbrook and Twist's mechanism. So, it enhances the reaction rate of cobalt based catalysts. [9]

For Co-B catalysts, it is found that addition of other elements like nickel [35], molybdenum [35,50] and phosphorous [37] or their combinations results higher activity. The reasons why these elements increase the activity of hydrogen generation from NaBH_4 can be listed as follows:

1. Elements like Ni, Fe increase the electron density of metallic Co sites.
2. Fe, Cu, Cr, Mo, W elements inhibit the Co agglomeration with supplying an increase in active surface area of catalyst.
3. The addition of elements like Cr, Mo, W which act as Lewis active site favors chemisorption of OH^- ions at the rate determining step.

Another important conclusion from Table 4 is the catalyst surface area plays an important role on the hydrogen generation rate. Liu et al. (2008) [30] reported very high activity of 26 L/min.g_{cat} with Co-B nonoparticles of 10nm in diameter. Their large surface area of catalyst yields high reaction rate, even higher than some noble metal catalysts and the reaction rate was reported to be first-order with respect to NaBH_4 concentration.

2.3.2 Transition Metal Salts

Besides to non-noble catalysts, metal salts can be used for accelerator of hydrolysis reaction. According to the research done by Schlesinger et al.[4] Co(II) chloride was found to be one of the most effective catalyst for hydrolysis of NaBH_4 . Nickel (II) chloride follows it in terms of activity while others such as iron (II), copper (II) and manganese (II) chlorides shows minimal activity.

Cobalt (II) chloride was forming a black precipitate when added to NaBH_4 solution. This black precipitate was determined as active catalyst and can be washed and re-used by retaining most of its activity. Another point is that in the

absence of boron metallic cobalt shows minimal activity hence boron enhances the reaction by acting as electron donor to Co active sites. [9]

Table 5 shows the selected studies conducted on transition of metal salts in literature. Maximum hydrogen generation rate (L/min) was reported per gram metal used in catalysts.

Table 5 Literature review on Transition of Metal Salts

| Year | Catalyst | HGR (L H ₂ /min/g _{met} al) | GHSC (wt%) | Yield (%) | Temp. (°C) |
|------------|----------------------------------|---|---------------|--------------|---------------|
| 1953, [4] | MnCl ₂ | <1.2 | 1.0 | <49 | 25 |
| 1953, [4] | FeCl ₂ | 1.7 | 1.0 | 65 | 25 |
| 2006, [53] | FeCl ₂ | 1.2 | 0.4 | 50 | 25 |
| 1953, [4] | CoCl ₂ | 3.7 | 1.0 | 97 | 25 |
| 2006, [53] | CoCl ₂ | 4.9 | 0.4 | 50 | 25 |
| 2006, [66] | CoCl ₂ | 0.6 | 0.2 | -- | 10 |
| 2009, [67] | CoCl ₂ | 11.4 | 6.8 | 92 | 20 |
| 1953, [4] | NiCl ₂ | 2.5 | 1.0 | 99 | 25 |
| 2006, [53] | NiCl ₂ | 2.5 | 0.4 | 50 | 25 |
| 2006, [66] | NiCl ₂ | <0.1 | 0.2 | -- | 20 |
| 2006, [66] | NiFe ₂ | <0.1 | 0.2 | -- | 50 |
| 1953, [4] | CuCl ₂ | 1.2 | 1.0 | 40 | 25 |
| 2006, [53] | RuCl ₃ | 85.4 | 0.4 | 50 | 25 |
| 2006, [53] | RhCl ₃ | 85.4 | 0.4 | 50 | 25 |
| 2006, [53] | PdCl ₂ | 0.1 | 0.4 | 50 | 25 |
| 2006, [53] | IrCl ₄ | 0.5 | 0.4 | 50 | 25 |
| 2006, [53] | H ₂ PtCl ₆ | 13.3 | 0.4 | 50 | 25 |

Liu et al. [66] compared the activities of cobalt chloride, nickel chloride and for the first time nickel fluoride. The highest reactivity belonged to cobalt salt but their performance was much lower than that obtained in Zahmakiran [53] and Schelisenger [4] works on same catalyst. This may be explained by the fact that Liu et al. [66] used stabilized aqueous solution with 10 wt% NaOH and slightly lower reaction temperature. [68]

The other conclusion from Table 5 is that noble metal based salts shows higher performance. Nevertheless, cobalt chloride appears to be promising because the price is cheaper than many noble metals. [68]

Also, it must be noted that there are limited data available for performance tests of ferric chloride in the hydrolysis of sodium borohydride.

2.3.3 Noble Metal Catalysts

Schlesinger et al. (1953) also found that platinum could be used to accelerate the hydrolysis of aqueous NaBH₄, although this was not the focus of their paper. Brown and Brown (1962) were the first to specifically investigate noble metal catalysts, prepared by reduction of noble metal chlorides like RuCl₃, RhCl₃ and H₂PtCl₄ in aqueous NaBH₄ solution.

Table 6 summarizes the researches done by using noble-metal catalysts.

Table 6 Literature review on Noble-Metal Catalysts

| Year | Catalyst | HGR (L H ₂ /min/g _{cat}) | HGR (L H ₂ /min/g metal) | NaBH ₄ Conc. (wt%) | NaOH Conc. (wt%) | Temp. (°C) |
|------------|-----------------------|---|-------------------------------------|-------------------------------|------------------|------------|
| 2000, [51] | Ru/IRA-400 | 0.19 | 3.77 | 20 | 10 | 25 |
| 2002, [52] | Pt/LiCoO ₂ | 3.10 | 206.5 | 20 | 10 | 22 |
| 2005, [53] | Ru nanoclusters | 96.8 | 96.8 | 0.75 | 0 | 25 |
| 2006, [54] | Pt/C | 23 | 175.57 | 10 | 5 | 25 |
| 2007, [55] | Ru/C | 0.77 | 12.9 | 1 | 3.75 | 25 |
| 2007, [56] | Rh/TiO ₂ | 1.82 | 360 | 0.5 | 0 | 40 |
| 2008, [57] | Ru/IR-120 | 0.13 | 13.2 | 5 | 1 | 25 |
| 2008, [58] | Ru-Fe-Co/AC | 5.03 | 41.73 | 10 | 4 | 25 |

Table 6 (cont'd) Literature review on Noble-Metal Catalysts

| | | | | | | |
|---------------|-----------------------------------|-------|-------|------|-----|----|
| 2009, [59] | Ru nanoclusters/z eolite | 0.13 | 16.13 | 1.1 | 5 | 25 |
| 2010, [60] | Ru/C (graphite) | 0.97 | 32.3 | 10 | 5 | 30 |
| 2010, [61] | Rh/TiO ₂ | 0.21 | 21 | 15 | 5 | 23 |
| 2011, [62] | Ni-Ru | 1.81 | 67 | 10 | 7 | 25 |
| 2012, [63] | Ru/Al ₂ O ₃ | 0.07 | 1.36 | 12.5 | 0.4 | 25 |
| 2013, [69] | Pt/C | 17.92 | 89.6 | 1.5 | 0.3 | 25 |
| 2016, [71] | Ni-Ru | 0.98 | 24.5 | 10 | 7 | 25 |

As can be seen from Table 6, ruthenium is the most investigated catalyst material. Amendola et al. (2000) used ruthenium (Ru) loaded on ion exchange resin IRA-400 as the sodium borohydride hydrolysis catalyst. [51] In the subsequent publications, different support materials like activated carbon, titanium, and LiCoO_2 and co-loading with other catalyst metals such as Ni and Pt. Many of these works have resulted in improved catalytic performance of Ru. [9]

An important issue with Ru catalyst is that activity of Ru catalysts was inversely proportional with the concentration of NaOH [9]. That is also reported for Pt/C catalysts on our previous work. [69]

The most active catalyst reported in Table 6 based on per unit mass of noble metal is Rh loaded on TiO_2 , as prepared by Simagina et al. (2007), with an activity of $360 \text{ LH}_2/\text{min}/\text{g}_{\text{metal}}$ [56]. However, this high activity may be partly due to the reaction temperature that is $40 \text{ }^\circ\text{C}$, which is $10\text{-}15 \text{ }^\circ\text{C}$ higher than most other catalysts reported in the table.

2.4 Sodium Borohydride Hydrolysis System Design

As explained in detail in Section 2.3, there are various types of catalysts available in literature for accelerating the hydrolysis reaction. Each work is valuable in terms of contributions to state of art of the sodium borohydride technology. But, there are still some open points that must be addressed before the commercialization of this system. First challenge is catalyst activity, catalyst durability and catalyst cost and heat management. Those works mentioned in Section 2.3 are trying to eliminate one or more of these issues related with the hydrolysis catalysts. Second challenge is the solubility of NaBO_2 in order not to block the system's pipelines. Precipitation of NaBO_2 causes irremediable drawbacks on operation of the system. Third issue is the cost of NaBH_4 production. More efforts should be paid to the development of new NaBH_4 synthesis process. The final and most important issue is the water management in the system. Since gravimetric hydrogen storage capacity (GHSC) is an important parameter for practical applications, a higher ratio of the weight of the system comes from water. Table 2.4 shows effect of "hydration factor" on GHSC based on theoretical calculations.

Table 7 Effect of hydration factor on gravimetric hydrogen storage capacity, GHSC [9]

| Hydration Factor,x | GHSC (wt%) |
|--------------------|------------|
| 0 | 10.8 |
| 2 | 7.3 |
| 4 | 5.5 |

So, as can be understood from Table 2.4, water amount must be optimized. This doctorate thesis aims to solve water management issue of sodium borohydride system by using solid state sodium borohydride.

Using solid sodium borohydride instead of introducing it as an aqueous solution stabilized with NaOH to the system promotes 3 main advantages listed as follows:

- i. Increases the gravimetric hydrogen storage capacity of sodium borohydride by using limited amount of water.
- ii. Decreases the system weight.
- iii. There is no need to use a separate storage fuel tank for storing the aqueous NaBH₄ solution. So, the number of equipment that is necessary for system design is reduced.

Figure 6 explains the remaining challenges of sodium borohydride system. So, these challenges together with the ones that are explained in section 2.2 must be solved for practical applications.

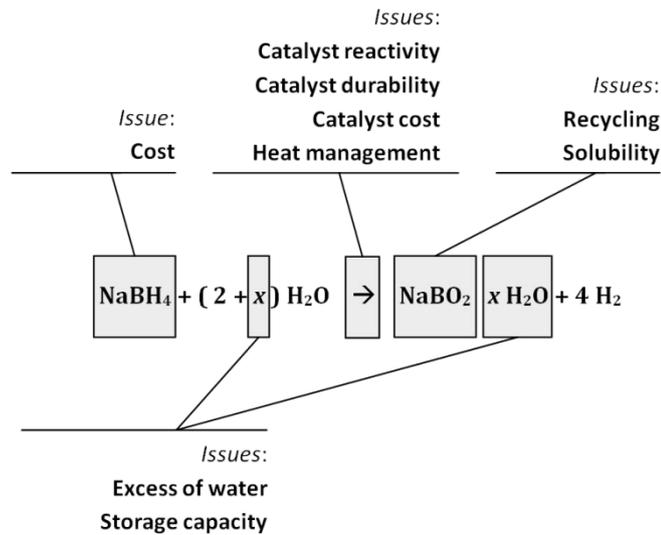


Figure 6 Issues on NaBH₄ hydrolysis [68]

In literature, throughout all studies, the main idea is to design a sodium borohydride hydrolysis reactor system together with fuel cell for commercial applications. Most of the continuous hydrolysis reactor systems in literature composed of a pump for transferring the fuel that is stabilized NaBH₄ solution to the reactor in which catalyst was placed. Reactor is followed by a H₂ separator in order to separate by-products. This system is illustrated in the work of Kojima et al. [70] and shown in Figure 7.

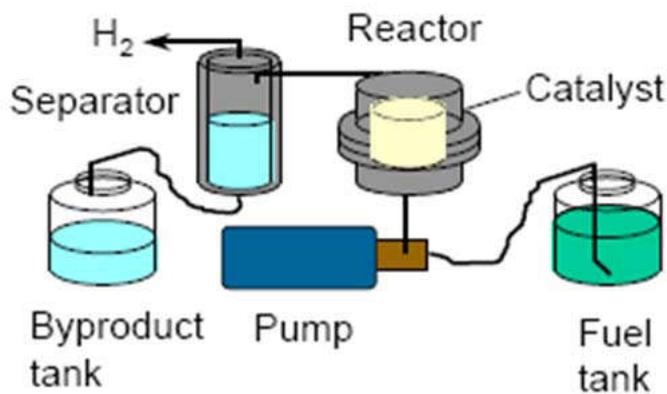


Figure 7 NaBH₄ storage system [70]

Table 8 summarizes the continuous NaBH₄ storage systems in literature.

Table 8 Literature review on continuous NaBH₄ storage system

| Year | NaBH ₄ (wt%) | NaOH (wt%) | Catalyst | Temp. (°C) | H ₂ Yield (%) | Comments | Ref. |
|------|----------------------------|---------------|-----------------------------------|---------------|-----------------------------|---|------|
| 2004 | 25 | 4 | Pt/LiCoO ₂ | 110 | 100 | Max H ₂ gen 120nL/min | [70] |
| 2005 | 20 | 10 | Ru/IRA- 400 | 25 | 98.9 | Cystallizati on problem | [8] |
| 2005 | 30 | 4 | Ru/Al ₂ O ₃ | n.i | 100 | Excess catalyst was used | [72] |
| 2005 | 25 | 1 | Ru | n.i | 100 | Clogging at high NaBH ₄ conc. | [73] |
| 2007 | 20 | 1 | Co-B/Ni foam | 105 | 76 | Yield decreases with NaBH ₄ conc. increase | [74] |
| 2007 | 15 | 3 | Ru/C | 100 | 100 | Blockage of flow channels | [75] |
| 2008 | 15 | 4 | PtRu/C | 46 | 100 | H ₂ yield decreases with flow rate increase | [76] |
| 2009 | 20 | 10 | Ru | 22 | 90 | Separation of NaBO ₂ needed | [77] |
| 2010 | 8 | 10 | Co powder | 22-38 | 84.2 | Conversion drooped | [78] |
| 2013 | 1.5 | 0.3 | Pt/C | 25 | 95 | Max H ₂ gen 980nL/min | [69] |

As can be seen from Table 8, in literature most of the continuous sodium borohydride systems were based on noble-metal catalysts and presented alkaline stabilized sodium borohydride solution.

In this doctorate thesis, we aim to contribute to the literature by purposing a system that is not alkaline stabilized and using cheap and effective FeCl_3 and CoCl_2 catalysts. This will be the first time of testing solid sodium borohydride system's performance in PEM fuel cell. In the following Section 2.5, brief introduction of fuel cell history and theory will be given.

The experimental scope will be given in Chapter 4. The results of kinetic experiments within this scope will be given as Chapter 5. The system integration with PEM fuel cell will be given in Chapter 6.

2.5 Fuel Cell Overview

2.5.1 Brief History of Fuel Cells

Fuel cells are electrochemical devices that convert chemical energy of fuel into electricity for commercial applications. The first invention of fuel cell operating principle was discovered by Sir William Grove in 1839 by the attribution of "gaseous fuels that generate electricity". However, this theory remains nothing more than a scientific curiosity over almost a century. In 1937, Francis T. Bacon started working on practical fuel cells and developed 6kW fuel cell by the end of 1950s. Fuel cells regain its attraction by the fuel cell applications in U.S. Space Program. In the beginning of 1960s, General Electric developed first polymer membrane (PEM) fuel cells in the Gemini Program. This was followed by Apollo Space Program that uses fuel cells licensed by Bacon's patents. Figure 8 shows the schematic picture of Apollo fuel cell. In the mid-1960s, General Motors tested a van operating with fuel cell. Perry Energy Systems worked with Ballard Company in order to demonstrate a PEM fuel cell powered submarine in 1989. In 1993, Ballard Power Systems experimented fuel cell operation for buses. A new industry was born as car companies began to support fuel cells and developed fuel cell-powered vehicles. The number of fuel cell related patents increases

dramatically by today showing a continuous interest in scientific and engineering community. [82]

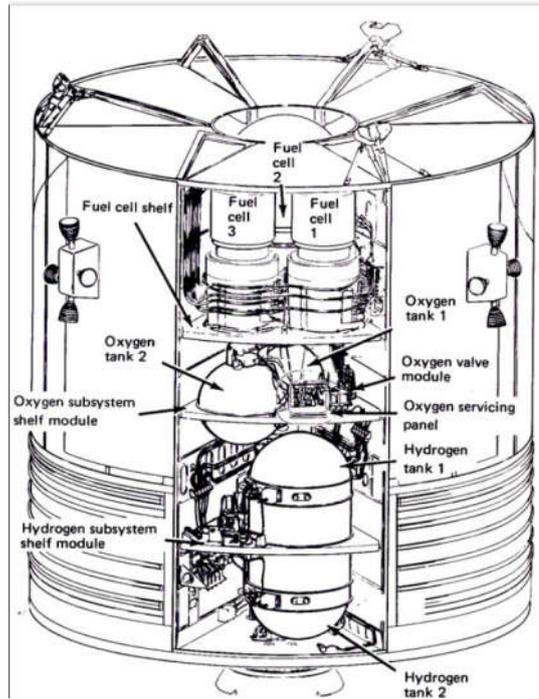


Figure 8 Apollo fuel cell [81]

2.5.2 Types of Fuel Cells

Fuel cells are named according to the type of electrolyte that they use as: Alkaline fuel cells (AFC), Polymer electrolyte membrane fuel cells. Phosphoric acid fuel cells (PAFC), Molten carbonate fuel cells (MCFC) and Solid oxide fuel cells (SOFC). Figure shows the types of fuels cells.

Alkaline fuel cells (AFC) use aqueous solution of potassium hydroxide as electrolyte. For high temperature operation ($250\text{ }^{\circ}\text{C}$), high concentration of KOH (85 wt%) is used whereas, for low temperature operations under $120\text{ }^{\circ}\text{C}$, low concentration of KOH (30-50 wt%) is required. In this type of fuel cells CO_2 must not be present in either fuel or oxidant. Ni, Ag, metal oxides can be used as electrocatalysts in these fuel cells. Alkaline fuel cells have been used in space applications. [82]

Polymer electrode membrane or proton exchange membrane fuel cells (PEMFC) use thin proton conductive polymer membrane most commonly used as perfluoro sulfonic acid as the electrolyte. Their operation temperature is 60-80 °C . They generally use platinum supported on carbon as electrocatalysts. Their solid electrolyte reduces the corrosion and provides quick start-up. However they are sensitive to fuel impurities. These types of fuel cells are considered as the most promising candidates for portable and vehicular applications. [82]

Phosphoric acid fuel cells (PAFC) use concentrated phosphoric acid as the electrolyte. They operates at high temperatures like 150-220 °C . Pt catalyst are used in both anode and cathode sides. In this type of fuel cells fuel impurities are not so critical. However, they require a long start up time. [82]

Molten carbonate fuel cells (MCFC) have alkali carbonates like Li, Na and K soaked in a ceramic LiAlO_2 matrix as electrolyte. They operates at a very high temperature range of 600-700 °C . They can use variety of catalyst hence, at high temperature noble metal catalysts are not required. They are typically used for stationary power generation. [82]

Solid oxide fuel cells (SOFC) use a solid, nonporous metal oxide as the electrolyte. This electrolyte is commonly Y_2O_3 stabilized ZrO_2 . Operating temperatures of these cells are 800-1000 °C . Operation at high temperatures causes corrosion of components of fuel cells and requires long start-up time. Like MCFC, SOFC are also used in stationary power generation. [82]

Figure 9 shows the important features of different types of fuel cells.

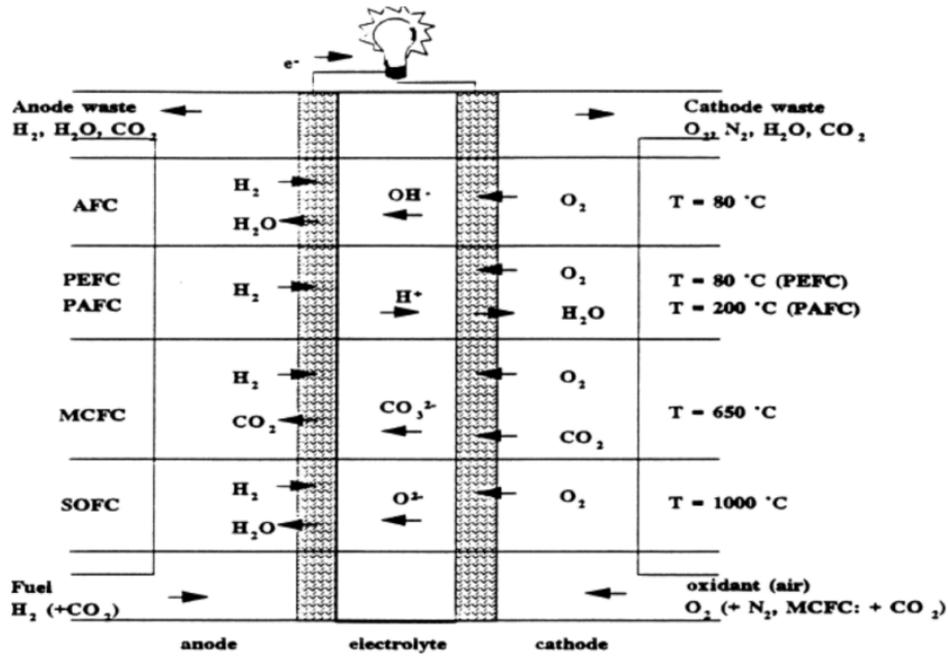


Figure 9 Different types of fuel cells

2.5.3 Basic Fuel Cell Theory

The basic electrochemical reactions occur at anode and cathode sides of fuel cell can be written as follows:

At the anode:



At the cathode:



Overall:



The overall reaction showed in equation 2.7 is the same reaction of hydrogen combustion. Thus, it is an exothermic reaction, its enthalpy is 286 kJ/mol at 25 °C [82].

Theoretical fuel cell potential can be expressed in terms of electrical work.

In general electrical work can be written as in Equation 2.8:

$$W_{el} = qE \quad (2.8)$$

where, W_{el} is the electrical work in units of J/mol, q is charge (Coulombs/mol) and E is the potential in units of Volts.

Total charge transferred in a fuel cell reaction per mole of H_2 consumed can be written as in Equation 2.9.

$$q = nN_{Avg}q_{el} \quad (2.9)$$

where:

n =number of electrons per molecule of H_2 that is 2 electrons per molecule.

N_{Avg} =number of molecules per mole that is Avogadro's number= 6.022×10^{23} molecules/mol

q_{el} =charge of one electron= 1.602×10^{-19} Coulombs/electron

The product of N_{Avg} and q_{el} is known as Faraday's constant (F) with the value of $F=96485$ Coulombs/electron/mol

The equations 2.8 and 2.9 can be combined together with the Faraday's constant as:

$$W_{el} = nFE \quad (2.10)$$

Also, the maximum amount of electrical energy generated in a fuel cell is the Gibbs free energy ($-\Delta G$).

So, the theoretical potential of fuel cell can be calculated as:

$$E = \frac{-\Delta G}{nF} = \frac{237,340 \text{ J/mol}}{2 \times 96,485 \text{ C/mol}} = 1.23 \text{ Volts} \quad (2.11)$$

So, at 25°C , the theoretical potential of a hydrogen/oxygen fuel cell is 1.23V. However, this ideal voltage cannot be reached due to the losses during fuel cell

operation. Deviation from the ideal behavior because of the total loss of the cell voltage can be categorized as: activation polarization loss, ohmic polarization loss, and the concentration polarization loss. The typical polarization curve containing all losses is shown in Figure 10. [82]

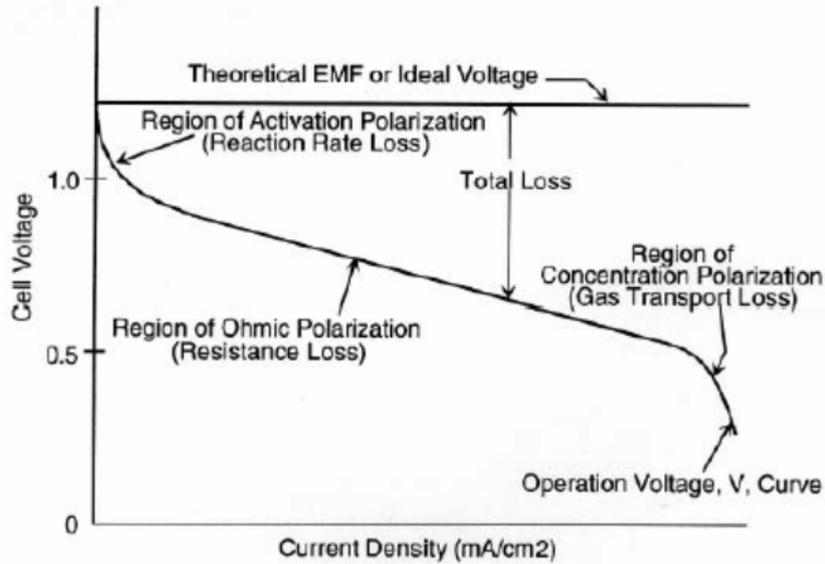


Figure 10 Typical polarization curve of a fuel cell [87]

The fuel cell hydrogen efficiency is defined as the ratio of electricity produced to hydrogen consumed.

$$\eta = \frac{W_{el}}{W_{H_2}} \quad (2.12)$$

W_{H_2} , that is energy value of hydrogen consumed ($J/s=W$) is directly related to the current according to the Faraday's law as follows:

$$W_{H_2} = \Delta H \frac{I}{nF} \quad (2.13)$$

where, ΔH is the hydrogen's higher heating value of 286kJ/mol.

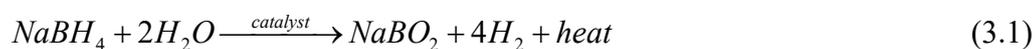
So, efficiency of the fuel cell is directly proportional to the cell voltage according to the Equation 2.14:

$$\eta = \frac{V}{1.482} \quad (2.14)$$

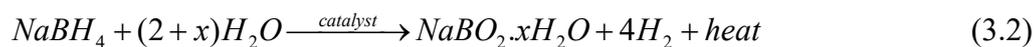
CHAPTER 3

CHEMISTRY OF THE PROCESS

The NaBH₄ hydrolysis reaction is shown in Equation 3.1.



If water is in excess, the reaction is expressed as in Equation 3.2.



where, x is called “*hydration factor*”. In excess water, one should consider the solubility of NaBH₄, NaBO₂ and the solid catalyst which is either FeCl₃ or CoCl₂ used in the present work.

Solubility of NaBH₄ and NaBO₂ in water were investigated by Kojima et al. [12] and in Chapter 2 their temperature dependency was shown in Equation 2.1 and 2.2 respectively.

Figure 11 shows the variation of the solubility of NaBH₄ and NaBO₂ with temperature as a graph.

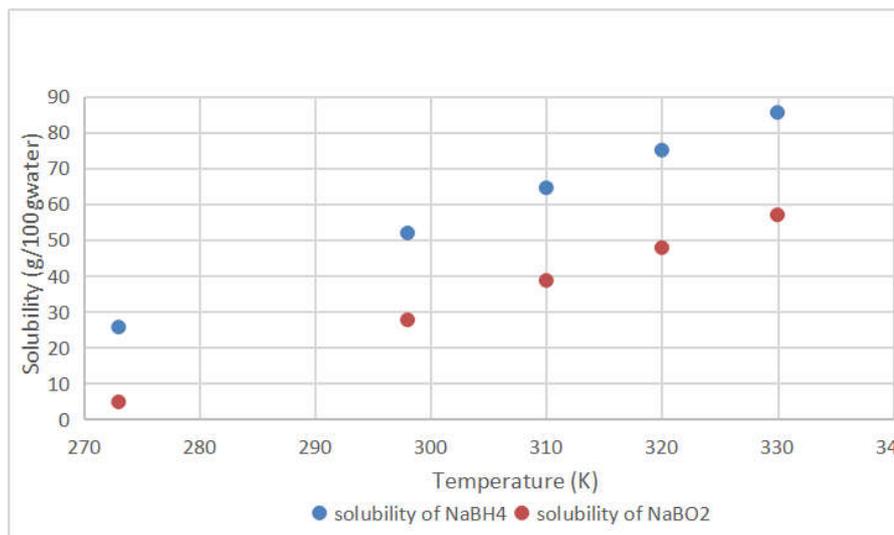


Figure 11 Solubility of NaBH₄ and NaBO₂ with temperature

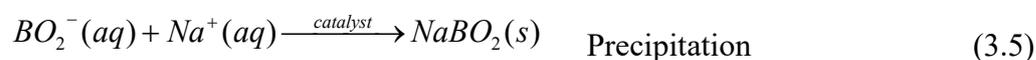
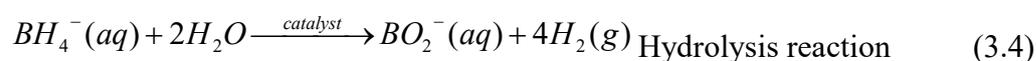
Hydrolysis reaction can occur without catalyst at a certain level called “self hydrolysis”. In order to suppress self hydrolysis of NaBH₄ in aqueous solutions alkaline medium is required.

Within the scope of this thesis, H₂ generation kinetics has been investigated with different amounts of solid NaBH₄, and water as reactants, FeCl₃ or CoCl₂ as catalyst.

There are two cases investigated in the present work:

1. The solid catalyst is mixed with NaBH₄ and placed in the reactor and then water is injected to the reactor to start the reaction.
2. The solid catalyst dissolved in water, only NaBH₄ is placed in the reactor and then catalyst- water solution is injected to the reactor to start the reaction

The chemistry of the two cases needs to be explained.



During the hydrolysis reaction catalysts also dissolved in water according to following reactions:

Dissolution of FeCl₃ catalyst:



Dissolution of CoCl₂ catalyst:



At 20 °C , the solubility of FeCl₃ in water is 920g/L, whereas the solubility of CoCl₂ in water is 530g/L.

In the reaction environment, Fe⁺³ and Co⁺² are reduced by electron transferred from BH₄⁻ ion to Fe⁺³ and Co⁺² as follows:

Reduction of FeCl₃ catalyst:

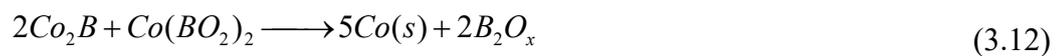
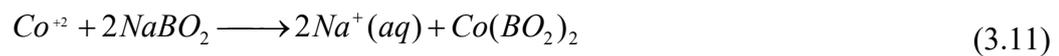
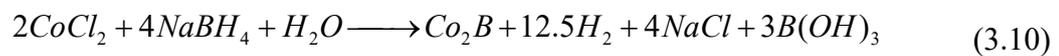


Reduction of CoCl₂ catalyst



Holbrook and Twist [10] mechanism is expected to occur for metallic Fe or Co. This metallic Fe and Co serve as active catalysts during hydrolysis reaction.

In literature, the reduction of CoCl₂ catalyst during the hydrolysis of NaBH₄ was reported as following reactions [80]:



As it is stated in Glavee's paper [84], "cobalt metal particles can only be obtained as a secondary product by adjusting conditions so that a mixture of Co₂B and

Co(BO₂)₂ is produced, and this solid mixture is forced to undergo a solid-state reaction to produce Co(s) and boron oxides” [84].

Up to our literature survey, there is no paper published on the reduction of FeCl₃ catalyst during the hydrolysis of NaBH₄.

CHAPTER 4

EXPERIMENTAL WORK

4.1 Materials, Catalysts and Experimental Procedure

Iron (III) chloride hexahydrate (FeCl_3) supplied from MERCK® and Cobalt (II) chloride hexahydrate (CoCl_2) were supplied from Carlo Erba Reagents® batch number of V5E550316H and solid state sodium borohydride (NaBH_4) (was supplied from National Research Institute of Boron (BOREN) with a purity of ≥ 96) was used in experiments. Bottled drinking water is used as reactant in most of the experiments. The specifications of water were given in Appendix E.

As a hydrogen generation reactor, three reactors having different dimensions which were made from tempered glass (WECK glass) was used. Reactor 1 (R1); had an internal volume of 80mL and cover diameter of 5.5 cm. Reactor 2 (R2); had an internal volume of 296mL and cover diameter of 9.5cm. Reactor 3 (R3); had an internal volume of 290mL and cover diameter of 7.5cm. Figure 12 shows the photograph of these three reactors used in hydrolysis of NaBH_4 experiments. The geometric specifications of reactors are given in Table 9.



Figure 12 Reactors used in hydrogen generation from hydrolysis of NaBH_4

Table 9 Geometric Specification of Hydrolysis Reactors

| Reactor Number | Length (cm) | Internal Volume (mL) | Cover Diameter (cm) | Bottom Diameter (cm) | Weight (g) (Reactor + cover) |
|----------------|-------------|----------------------|---------------------|----------------------|------------------------------|
| Reactor 1 (R1) | 4.5 | 80 | 6.5 | 5.0 | 138 |
| Reactor 2 (R2) | 7.0 | 290 | 9.5 | 8.5 | 370 |
| Reactor 3 (R3) | 8.5 | 290 | 7.5 | 6.0 | 255 |

For hydrogen generation from solid state NaBH_4 hydrolysis an experimental setup composed of 4 main parts which are; hydrolysis reactor, gas-liquid separator (made from glass with volume of 200mL and weight of 74g), mist eliminator (containing approximately 20g of glass wool with total weight of 65g) in order to prevent the liquid drops coming from reactor and finally mass flow meter (Bürkert®, Model No: 8705) that has maximum hydrogen flow rate of 3L/min was constructed. Mass flow meter was connected to the computer with RS485. So, H_2 generation flow rate was directly measured and monitored online by using

Reliance 5.0 program. H_2 generation rate was recorded in every 1 second. Figure 13 shows the photograph of the experimental setup.

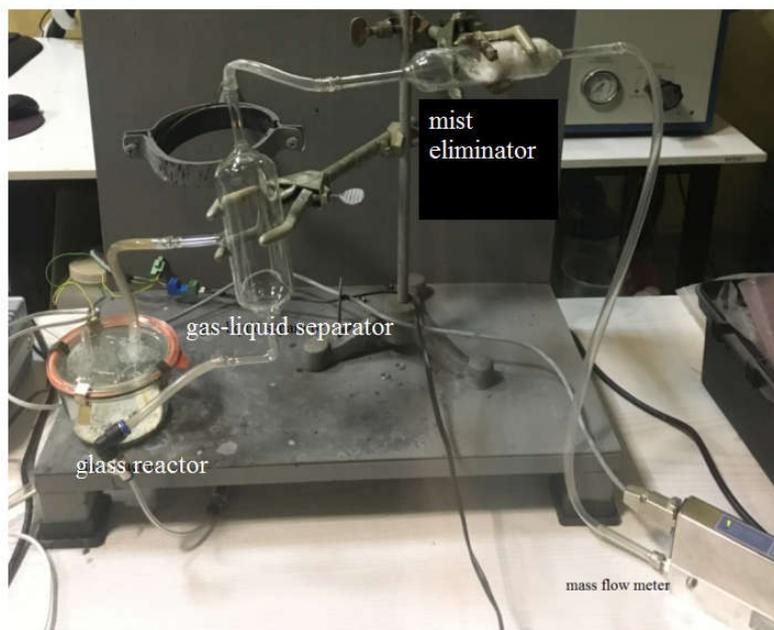


Figure 13 Photograph of experimental setup for hydrolysis of $NaBH_4$

As explained in Chapter 3, two different procedures were applied for start-up of hydrogen generation from hydrolysis of $NaBH_4$ experiments. In the first case, Case 1, desired amount of solid $NaBH_4$ and solid catalyst were placed in the reactor. Required quantity of water at room temperature was injected directly into the reactor with a syringe that has a volume of 100mL in order to initiate the hydrolysis reaction. H_2 generation rate was monitored after the injection of water. In the second case, Case 2, only the desired amount of solid $NaBH_4$ was placed in the reactor. The solid catalyst was dissolved in the desired amount of water and catalyst solution was obtained. This catalyst solution at room temperature was injected with a syringe (100mL) into the reactor which contains only solid $NaBH_4$. H_2 generation rate was monitored starting with the injection of catalyst solution.

In all of the experiments, temperature of the reactor contents was neither tried to be keep constant nor monitored. In all of the experiments mechanical or magnetic stirring was not applied. Moreover, the data for reproducibility experiments (repeated 3 times) is given in Appendix 4.

4.2 Scope of Experiments

4.2.1 Scope of Kinetic Experiments

Each experimental condition including the runs and experimental parameters are shown in Table 10. The experiments were conducted in three different reactor size and dimension (Specifications are given in Table 9). R1, R2 and R3 indicate the Reactor 1, Reactor 2 and Reactor 4 respectively.

Furthermore, as a reactant, bottled water was used in most of the experiments. Only, for experiments R3-18, R3-19 and R3-20; bottled, tap or 2ms ultra-pure de-ionized water was used to investigate the effect of water type.

Table 10 Experiments conducted on H₂ generation from hydrolysis of solid NaBH₄

Table 10(a) Experiments conducted on stoichiometric amount of water

| REACTOR 1 (R1) | | | |
|--------------------------|------------------------------------|------------------------------|------------------------------|
| Experiment Number | NaBH₄ Amount (g) | H₂O Amount | Catalyst |
| R1-1 | 5.0g | 4.8g, x=0 | no catalyst |
| R1-2 | 5.0g | 4.8g, x=0 | 0.1g solid FeCl ₃ |
| R1-3 | 5.0g | 4.8g, x=0 | 0.3g solid FeCl ₃ |
| R1-4 | 5.0g | 4.8g, x=0 | 0.5g solid FeCl ₃ |
| R1-5 | 5.0g | 4.8g, x=0 | 0.7g solid FeCl ₃ |
| REACTOR 2 (R2) | | | |
| R2-1 | 5.0g | 4.8g, x=0 | 0.5g solid FeCl ₃ |
| R2-2 | 10g | 9.50g, x=0 | 0.5g solid FeCl ₃ |
| R2-3 | 10g | 9.50g, x=0 | 1.0g solid FeCl ₃ |
| R2-5 | 20g | 19.0g, x=0 | 0.5g solid FeCl ₃ |
| R2-6 | 20g | 19.0g, x=0 | 1g solid FeCl ₃ |

Table 10(b) Experiments Conducted on Reactor 2

| REACTOR 2 (R2) | | | |
|--------------------------|------------------------------------|------------------------------------|------------------------------|
| Experiment Number | NaBH₄ Amount (g) | H₂O Amount | Catalyst |
| R2-4 | 10g | 19.0g, x=2 | 1.0g solid FeCl ₃ |
| R2-7 | 5.0g | 4.8g, x=0 | 1.0g solid FeCl ₃ |
| R2-8 | 5.0g | 9.5g, x=2 | 1.0g solid FeCl ₃ |
| R2-9 | 5.0g | 14.27g, x=4 | 1.0g solid FeCl ₃ |
| R2-10 | 5.0g | 3 times successive 4.8g, total x=4 | 1.0g solid FeCl ₃ |
| R2-11 | 5.0g | 23.8g, x=8 | 1.0g solid FeCl ₃ |
| R2-12 | 5.0g | 33.3g, x=12 | 1.0g solid FeCl ₃ |
| R2-13 | 5.0g | 42.8g, x=16 | 1.0g solid FeCl ₃ |
| R2-14 | 5.0g | 52.3g, x=20 | 1.0g solid FeCl ₃ |
| R2-15 | 10g | 4.8g, x=0 | 0.3g solid FeCl ₃ |
| R2-16 | 10g | 9.5g, x=0 | 1.0g solid FeCl ₃ |
| R2-17 | 10g | 9.5g, x=0 | 0.3g solid CoCl ₂ |

Table 10(c) Experiments conducted in Reactor 3

| REACTOR 3 (R3) | | | |
|---|------------------------------------|------------------------------|------------------------------|
| <i>water effect on solid FeCl₃ experiments</i> | | | |
| Experiment Number | NaBH₄ Amount (g) | H₂O Amount | Catalyst |
| R3-1 | 5.0g | 4.8g, x=0 | 0.5g solid FeCl ₃ |
| R3-2 | 5.0g | 14.4g, x=4 | 0.5g solid FeCl ₃ |
| R3-3 | 5.0g | 23.8g, x=8 | 0.5g solid FeCl ₃ |
| R3-4 | 5.0g | 33.3g, x=12 | 0.5g solid FeCl ₃ |
| R3-5 | 5.0g | 42.8g, x=16 | 0.5g solid FeCl ₃ |
| R3-6 | 5.0g | 52.3g, x=20 | 0.5g solid FeCl ₃ |
| R3-7 | 5.0g | 4.76g, x=0 | 1g solid FeCl ₃ |
| R3-8 | 5.0g | 14.3g, x=4 | 1g solid FeCl ₃ |
| R3-9 | 5.0g | 23.8g, x=8 | 1g solid FeCl ₃ |
| R3-10 | 5.0g | 33.3g, x=12 | 1g solid FeCl ₃ |
| R3-11 | 10g | 9.5g, x=0 | 0.3g solid FeCl ₃ |
| R3-12 | 10g | 9.5g, x=0 | 1g solid FeCl ₃ |
| R3-13 | 10g | 28.5g, x=4 | 1g solid FeCl ₃ |
| R3-14 | 10g | 66.6g, x=16 | 0.5g solid FeCl ₃ |

Table 10(c) (cont'd) Experiments conducted in Reactor 3

| <i>catalyst effect on solid FeCl₃</i> | | | |
|--|------------------------|-----------------------------------|-------------------------------|
| R3-15 | 5.0g | 42.8g, x=16 | 0.4g solid FeCl ₃ |
| R3-16 | 5.0g | 42.8g, x=16 | 0.6g solid FeCl ₃ |
| R3-17 | 5.0g | 42.8g, x=16 | 0.7g solid FeCl ₃ |
| <i>type of water effect on solid FeCl₃</i> | | | |
| R3-18 | 5.0g NaBH ₄ | 33.3g, x=12, bottled water | 0.5g solid FeCl ₃ |
| R3-19 | 5.0g | 33.3g, x=12, tap water | 0.5g solid FeCl ₃ |
| R3-20 | 5.0g | 33.3g, x=12, 2ms de-ionized water | 0.5g solid FeCl ₃ |
| <i>water effect on liquid FeCl₃ experiments</i> | | | |
| R3-21 | 5.0g | 4.8g, x=0 | 0.5g liquid FeCl ₃ |
| R3-22 | 5.0g | 14.3g, x=4 | 0.5g liquid FeCl ₃ |
| R3-23 | 5.0g | 23.8g, x=8 | 0.5g liquid FeCl ₃ |
| R3-24 | 5.0g | 33.3g, x=12 | 0.5g liquid FeCl ₃ |
| R3-25 | 5.0g | 42.8g, x=16 | 0.5g liquid FeCl ₃ |
| R3-26 | 5.0g | 52.3g, x=20 | 0.5g liquid FeCl ₃ |
| R3-27 | 10g | 9.5g, x=0 | 1g liquid FeCl ₃ |
| R3-28 | 10g | 28.5g, x=4 | 1g liquid FeCl ₃ |

Table 10(c) (cont'd) Experiments conducted in Reactor 3

| | | | |
|---|-----|-------------|-------------------------------|
| R3-29 | 10g | 47.6g, x=8 | 1g liquid FeCl ₃ |
| R3-30 | 10g | 66.6g, x=12 | 1g liquid FeCl ₃ |
| <i>catalyst effect on liquid FeCl₃ experiments</i> | | | |
| R3-31 | 10g | 66.6g, x=12 | 0.5g liquid FeCl ₃ |
| R3-32 | 10g | 66.6g, x=12 | 0.7g liquid FeCl ₃ |
| R3-33 | 10g | 9.5g, x=0 | 0.3g liquid FeCl ₃ |
| R3-34 | 10g | 9.5g, x=0 | 1g liquid FeCl ₃ |

4.2.2 Scope of Integration with PEMFC

The developed solid NaBH₄ hydrolysis system is integrated with PEMFC and tested for the performance by using the optimum condition that was obtained as a result of kinetic experiments. For fuel cell tests, a newly prepared MEA was also tested.

CHAPTER 5

RESULTS AND DISCUSSION OF KINETIC EXPERIMENTS

5.1 Effect of Solid FeCl₃ Catalyst on Reaction Rate at Stoichiometric Ratio of Reactants in R1

In reactor 1 (R1), experiments are conducted on stoichiometric amount of NaBH₄ and water ratio. As a startup procedure Case 1 was applied as explained in Chapter 4.1. 5g solid NaBH₄ and solid FeCl₃ catalyst; 0.1 g for R1-2, 0.3g for R1-3, 0.5g for R1-4 and 0.7g for R1-5 were placed inside the reactor. Stoichiometric amount of bottled water (hydration factor, x=0), 4.8 g was directly injected into the reactor. In R1-1, no catalyst was used.

Figure 14 shows the variation of H₂ generation rate with time for different amounts of solid FeCl₃ catalyst.

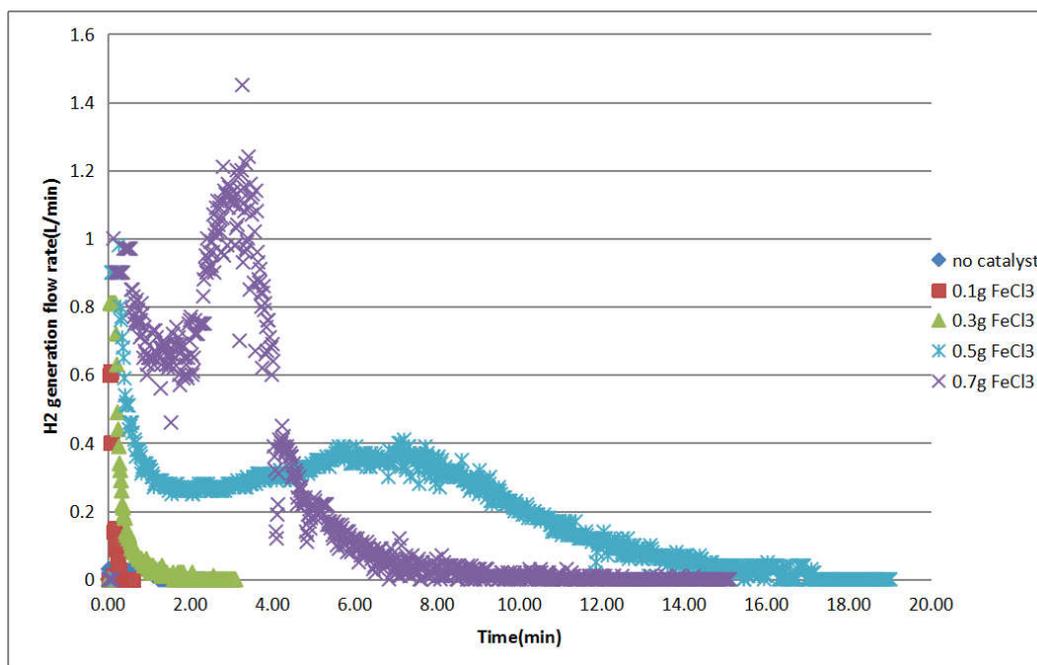


Figure 14 Variation of hydrogen generation rate with time at stoichiometric ratio of NaBH_4 and water for different amounts of solid FeCl_3 catalyst ($\text{NaBH}_4=5\text{g}$, $\text{H}_2\text{O}=4.8\text{g}$ $x=0$)

In R1-1, when there was no-catalyst, H_2 generation occurs with a very slow rate. Therefore, catalyst is needed in order to obtain higher flow rates. In R1-2 and R1-3, FeCl_3 amount was used as 0.1g and 0.3g respectively. The H_2 generation rate was below 0.2 L/min for both of the R1-2 and R1-3 and reaction was lasted in 3 minutes for R1-3. However, in R1-4, when solid FeCl_3 was used as 0.5g, H_2 generation was continued at a stable flow rate of 0.3L/min up to 6 minutes. At 7 minutes, it reached to a maximum flow rate of 0.4 L/min and then started to decrease. Reaction was lasted at 19 minutes. In R1-5, 0.7g of FeCl_3 was used; H_2 generation flow rate was reached to maximum of 1.2L/min at 3 minutes. As solid FeCl_3 amount increases, it results a quicker response time for obtaining higher H_2 generation rates. Therefore, catalyst amount has an important role in rate behavior.

“ H_2 Generation Yield” was defined as liter of H_2 produced per grams of NaBH_4 according to the Equation 5.1. Sample calculation is shown in Appendix A.

$$\text{Yield} = \frac{\text{Total } \text{H}_2 \text{ produced(L)}}{\text{Amount of } \text{NaBH}_4(\text{g})} \quad (5.1)$$

“Efficiency %” was defined according to Equation 5.2. Sample calculation for Efficiency % was shown in Appendix B.

$$\text{Efficiency}(\%) = \frac{\text{Total } H_2 \text{ Generated}(L)}{\text{Theoretical } H_2 \text{ Generated}(L)} \times 100 \quad (5.2)$$

Mean H_2 generation rate is was calculated from Equation 5.3 as follows where t_1 is duration:

$$\text{Mean } H_2 \text{ generation rate} = \frac{\text{Total } H_2 \text{ produced}(@t = t_1)}{\text{Duration}(t_1)} \quad (5.3)$$

Figure 15 illustrates the total amount of H_2 generated in liters with respect to time for different amounts of solid $FeCl_3$ catalyst.

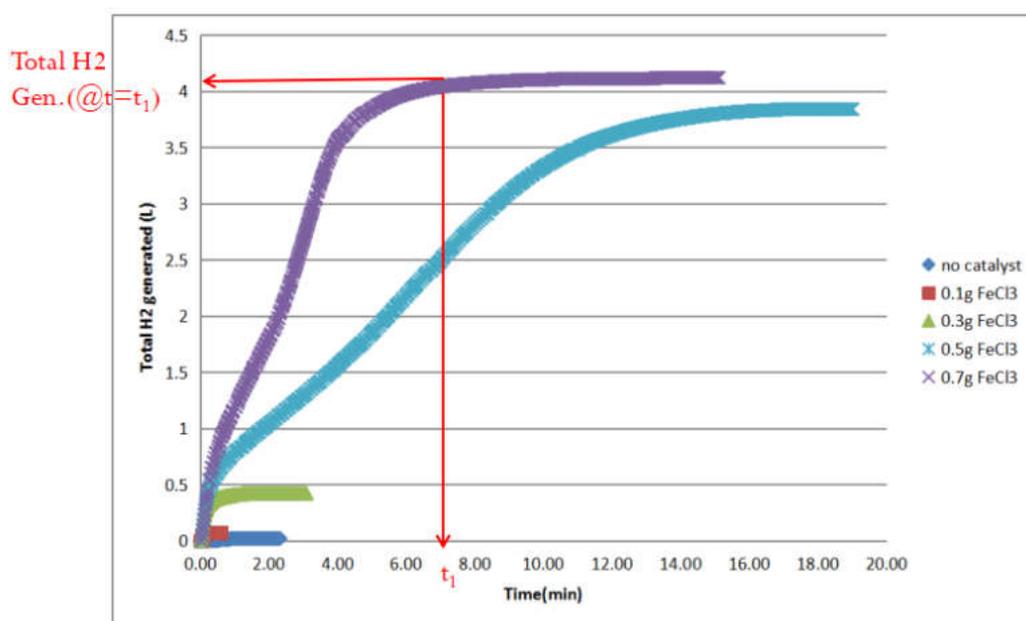


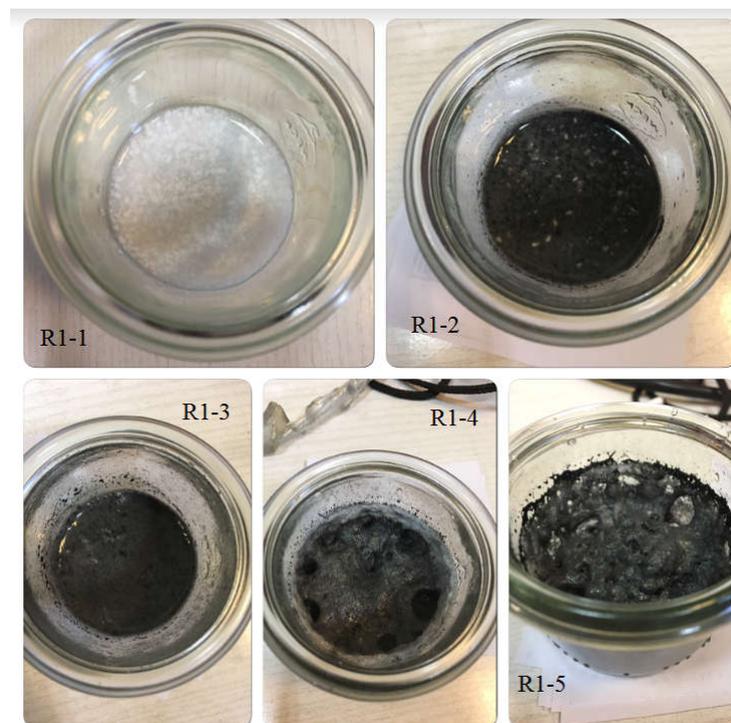
Figure 15 Variation of total amount of H_2 generated rate with respect to time at stoichiometric ratio of $NaBH_4$ and water for different amounts of solid $FeCl_3$ catalyst ($NaBH_4=5g$, $H_2O=4.76g$, $x=0$)

As shown in Figure 15, as solid $FeCl_3$ amount increases the total amount of H_2 generation increases.

Figure 16(a) illustrates the picture of the reactor contents before the reaction for R1-2, R1-3, R1-4 and R1-5. Figure 16(b) shows the picture of reactor contents after the reaction ends.



(a)



(b)

Figure 16 (a) Picture of reactor contents for R1-2,3,4,5 before the reaction
(b) Reactor contents after the reaction.

Table 11 shows the results of experiments conducted in Reactor 1.

Table 11 Results of the experiments conducted on Reactor 1 at stoichiometric ratio of NaBH₄ to H₂O (x=0, 5g NaBH₄, 4.80g H₂O)

| Experiment Number | Solid FeCl ₃ amount (g) | Total H ₂ Generated (L) | Duration (min) | Mean H ₂ generation rate (L/min) | Yield (L H ₂ /g NaBH ₄) | Efficiency % |
|-------------------|------------------------------------|------------------------------------|----------------|---|--|--------------|
| R1-1 | No catalyst | 0.02 | 1.2 | 0.02 | 0.004 | 0.17 |
| R1-2 | 0.10 | 0.07 | 0.5 | 0.14 | 0.014 | 0.59 |
| R1-3 | 0.30 | 0.42 | 1.9 | 0.22 | 0.084 | 3.55 |
| R1-4 | 0.50 | 3.78 | 15.6 | 0.24 | 0.756 | 31.92 |
| R1-5 | 0.70 | 4.12 | 7.1 | 0.57 | 0.824 | 34.79 |

From Table 11, it was concluded that when catalyst amount increases, efficiency increases. As can be seen from Figure 16, FeCl₃ catalyst has a yellow color initially but, with hydrolysis reaction it changes its color to black. These phenomena can be explained with the dissolution of FeCl₃ in water as described in Chapter 3, Equation 3.6. In R1-1, since there was no catalyst it stayed as white color.

Furthermore, as can be understood from Figure 16, when catalyst amount increases the reactor contents after the reaction got more solid (rigid) form rather than stayed in aqueous form. The coagulation of the byproduct sodium metaborate causes clogging of pipe if the reactor volume is not enough to keep all reactor contents in the reactor. Since glass reactor was used, during the hydrolysis reaction it was observed that volume of the reactor contents were increasing due to the formation of H₂ bubbles. So, the volume of the reactor is a critical parameter for keeping the byproduct, and unreacted reactants and catalyst inside the reactor during the reaction. Since R1 has a volume of 80mL which is not

enough to investigate further parameters on H₂ generation rate, reactor volume is increased.

5.2 Effect of NaBH₄ amount on H₂ generation rate at stoichiometric ratio of Reactants in R2

In Reactor 2 (R2), as a start-up procedure Case 1 was applied as explained in Chapter 4.1. For R2-1, 5g of NaBH₄, for R2-2 10g of NaBH₄, for R2-5 20g of NaBH₄ was placed in a reactor as solid form together with 0.5g of solid FeCl₃ catalyst. Stoichiometric amount of water that is; for R2-1, 4.76g of H₂O, for R2-2, 9.5g of H₂O and for R2-5, 19.0g of H₂O was injected directly into the reactor in order to initiate the H₂ generation. Figure 17 shows the variation of H₂ generation flow rate with respect to time.

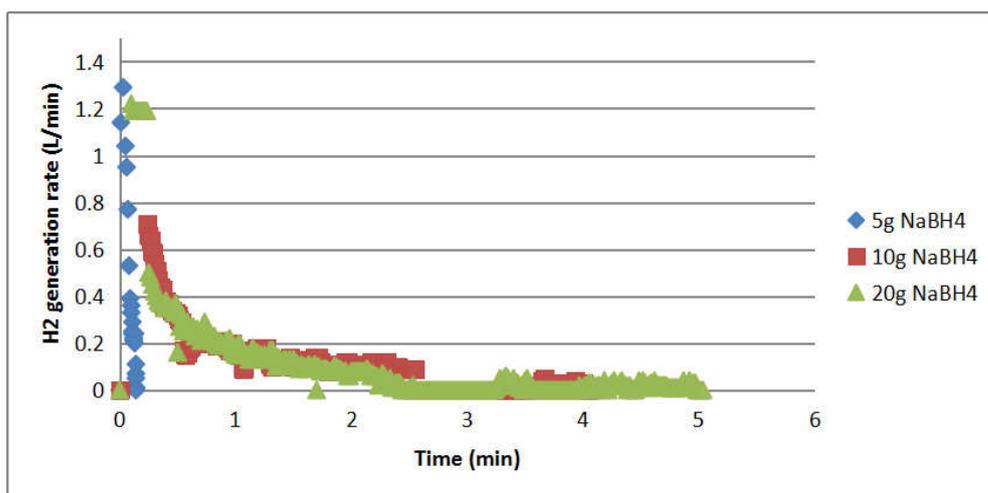


Figure 17 Variation of H₂ generation rate with time at stoichiometric ratio of NaBH₄ and water for various amounts of NaBH₄ (x=0, 0.5g solid FeCl₃ catalyst)

As shown in Figure 17, all experiments R2-1, R2-2 and R2-5 exhibit the same type of H₂ generation rate behavior under stoichiometric amount of H₂O introduced into the system. For R2-1, after injection of H₂O, H₂ generation rate rapidly decreased and for R2-2 and R2-5 the rate continued to decrease until 5 minutes. Different

than in R1-4 and R1-5 they did not show a maximum H_2 generation rate after certain time.

Figure 18 illustrates the total amount of H_2 generated with respect to time.

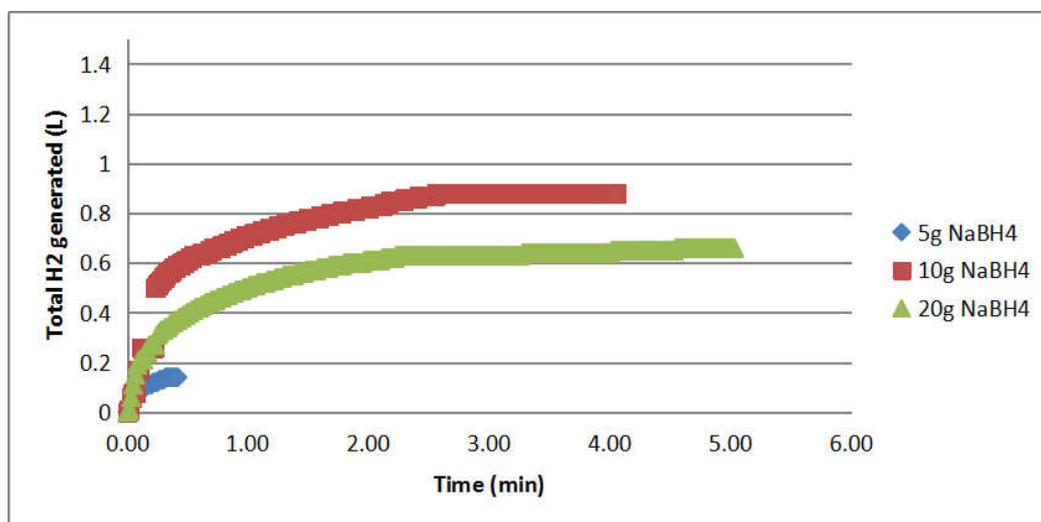


Figure 18 Total amount of H_2 generated with respect to time at stoichiometric ratio of $NaBH_4$ and water for different amounts of $NaBH_4$ ($x=0$, 0.5g solid $FeCl_3$ catalyst)

Yield and efficiency values were calculated according to the Equation 5.1 and Equation 5.2 respectively.

Figure 19 shows the picture of reactor contents after the hydrolysis reaction for R2-1, R2-2 and R2-5.

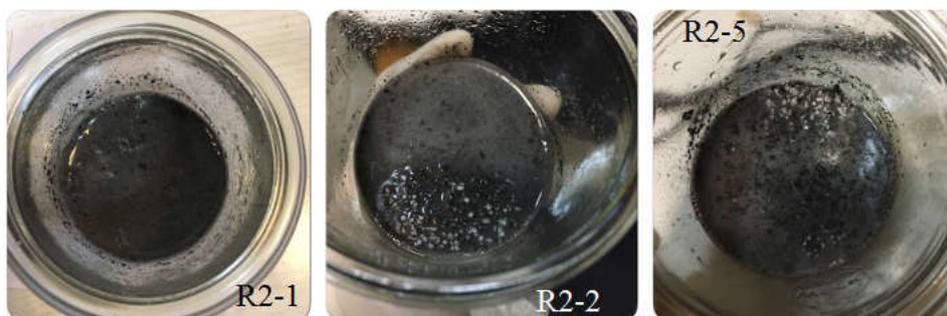


Figure 19 Picture of the reactor contents after the hydrolysis reaction

Table 12 shows the results of experiments conducted on Reactor 2 with hydration factor of $x=0$ for different amounts of NaBH_4 .

Table 12 Results of the experiments conducted on Reactor 2 (R2) at stoichiometric ratio of NaBH_4 to H_2O ($x=0$) for different NaBH_4 amounts

| Experiment Number | NaBH_4 amount (g) | H_2O amount (g) | Solid FeCl_3 amount (g) | Total H_2 Generated (L) | Yield (L H_2 /g NaBH_4) | Efficiency % |
|-------------------|----------------------------|---------------------------------|----------------------------------|----------------------------------|--|--------------|
| R2-1 | 5.0 | 4.80 | 0.50 | 0.14 | 0.028 | 1.18 |
| R2-2 | 10.0 | 9.50 | 0.50 | 0.88 | 0.088 | 3.71 |
| R2-5 | 20.0 | 19.0 | 0.50 | 0.66 | 0.033 | 1.39 |

For all R2-1, R2-2 and R2-5 efficiency values were too low. It does not mean that NaBH_4 has no effect on hydrolysis reaction. But, this is due to the fact that NaBH_4 may not find enough water to react and reveal all of its H_2 content (See Chemistry of the process Equation 3.1). Also, as can be seen from Figure 19, there were some NaBH_4 particles left un-dissolved after the reaction. It can be concluded that excess water is necessary for sustaining hydrolysis reaction.

5.3 Effect of hydration factor on H_2 generation rate in R2

In order to investigate the effect of water on H_2 generation rate, Case 1 as described in Chapter 4.1 was applied for start-up of the hydrolysis reaction. 5g of solid NaBH_4 and 1g of solid FeCl_3 were placed inside the R2. For R2-7, 4.8g of H_2O ($x=0$), for R2-8, 9.5g of H_2O ($x=2$), for R2-9, 14.3g H_2O ($x=4$), for R2-11, 23.8g of H_2O ($x=8$), for R2-12, 33.3g H_2O ($x=12$), for R2-13, 42.8g H_2O ($x=16$) and finally for R2-14, 52.3g H_2O ($x=20$) was injected directly into the R2. Figure 20 shows the variation of H_2 generation flow rate with respect to time for different hydration factors.

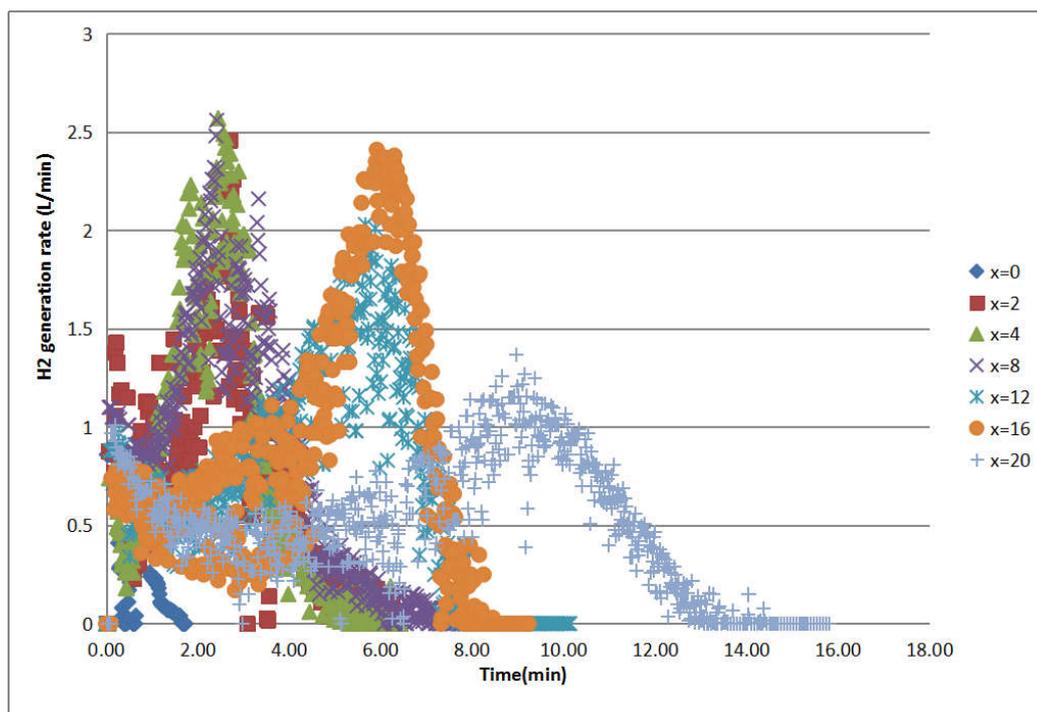


Figure 20 H₂ generation rate change with respect to time for different x values (NaBH₄=5g, solid FeCl₃ catalyst=1.0g)

According to the Figure 20, it can be seen that H₂ generation rate behavior was like “reversed-V” shape in all of the experiments. Although, the same amount of NaBH₄ and stoichiometric amount of H₂O were used as in R2-1, because of catalyst amount increased to 1.0g, “reversed-V” shape behavior was observed also in R2-7. In R2-7, maximum H₂ generation rate was obtained as 0.92 L/min at 0.7 minutes. At 3 minutes, R2-8, R2-9, R2-11 gave a maximum H₂ generation rate of 2.5L/min, 2.6 L/min and 2.6 L/min respectively. When x=12 for R2-12 and x=14 for R2-13, the maximum H₂ generation rate was obtained as 2.0 and 2.4 respectively at both around 6 minutes. Different from these experiments, R2-14 for x=20 gave broader “reversed-V” shape behavior with maximum H₂ generation rate of 1.3 L/min at 9 minutes. It was concluded that H₂O amount plays an important role on H₂ generation rate.

Figure 21 illustrates the change of total H₂ generation amounts with time for different hydration factors.

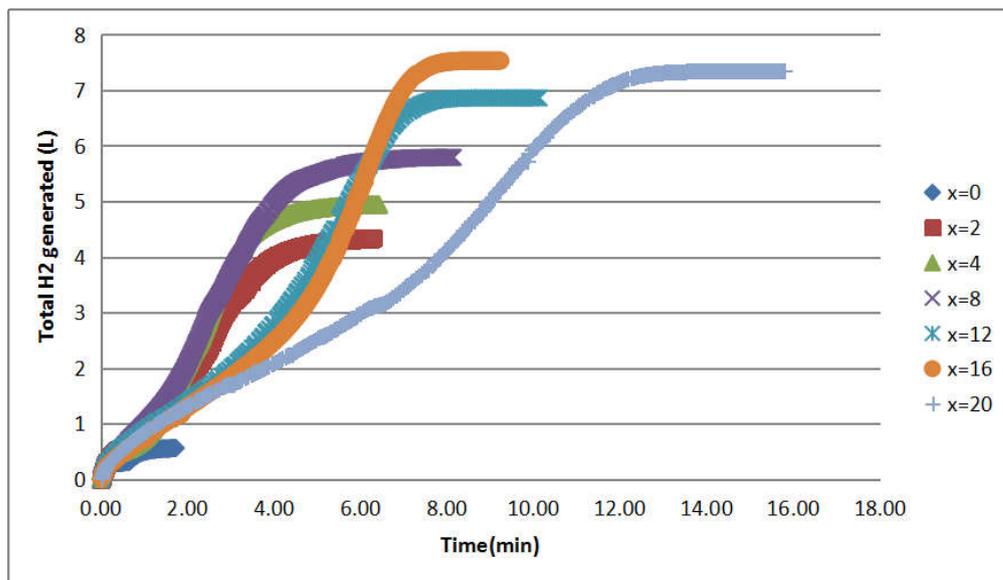


Figure 21 Change of total amount of H₂ produced with time for different hydration factors, x. (NaBH₄=5g, solid FeCl₃ catalyst=1.0g)

Figure 22 shows the picture of reactor contents after the reaction.

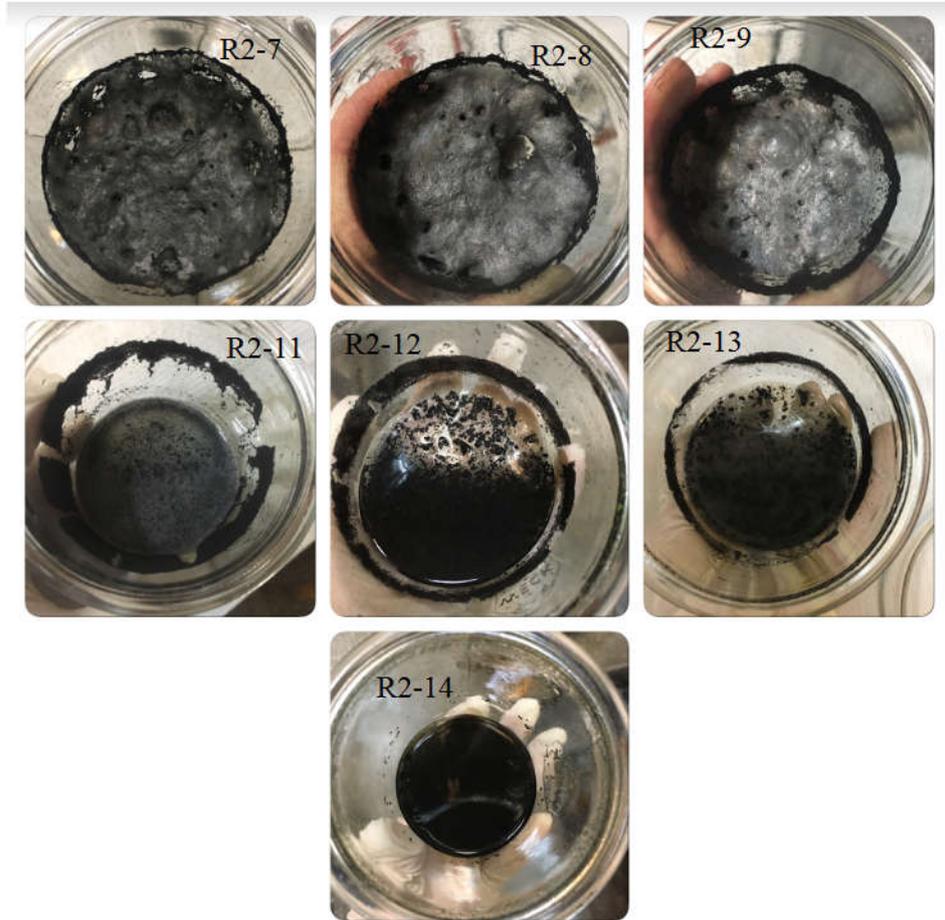


Figure 22 Contents of the reactor after the hydrolysis reaction

Table 13 summarizes the results of the experiments conducted in R2 for the effect of water on H_2 generation rate.

Table 13 Results of the experiments conducted on Reactor 2 (R2) at different hydration factors, x (5g NaBH₄, 1.0 g solid FeCl₃)

| Experiment Number | H ₂ O amount | Duration (min) | Mean H ₂ generation rate (L/min) | Total H ₂ Generated (L) | Yield (L H ₂ /g NaBH ₄) | Efficiency % |
|-------------------|-------------------------|----------------|---|------------------------------------|--|--------------|
| R2-7 | 4.8g, x=0 | 1.2 | 0.44 | 0.56 | 0.112 | 4.33 |
| R2-8 | 9.5g, x=2 | 4.5 | 0.92 | 4.34 | 0.868 | 33.57 |
| R2-9 | 14.3g, x=4 | 4.5 | 1.07 | 4.94 | 0.988 | 38.21 |
| R2-11 | 23.8g, x=8 | 6.1 | 0.94 | 5.79 | 1.158 | 44.79 |
| R2-12 | 33.3g, x=12 | 7.5 | 0.90 | 6.86 | 1.372 | 53.07 |
| R2-13 | 42.8g, x=16 | 7.9 | 0.95 | 7.53 | 1.506 | 58.25 |
| R2-14 | 52.3g, x=20 | 12.7 | 0.57 | 7.34 | 1.468 | 56.78 |

From Table 13, as hydration factor increases up to 16, hydrogen generation efficiency and yield also increases. Further increase in hydration factor resulted a decrease in efficiency. Moreover, as can be seen from Figure 22, as H₂O amount increases, the reactor contents stayed as in aqueous form. Crystallization or solidification of reactor contents had not been observed at x=8 and above x=8.

5.4 Effect of successive stoichiometric loading of H₂O on H₂ generation rate in R2

For R2-10, 5 g of NaBH₄ and 1 g of FeCl₃ were placed into the R2. At time=0, initially stoichiometric amount of H₂O (4.8g) was injected directly into the reactor in order to initiate the hydrolysis reaction. After, the reaction was finished; again 4.8g of H₂O was injected into the reactor without removing the reactor contents. When the reaction after the second injection of water finished, 3rd stoichiometric amount of water was given into the system. Figure 23 shows the variation of H₂ generation rate with time for successive injections of H₂O without interrupting the system.

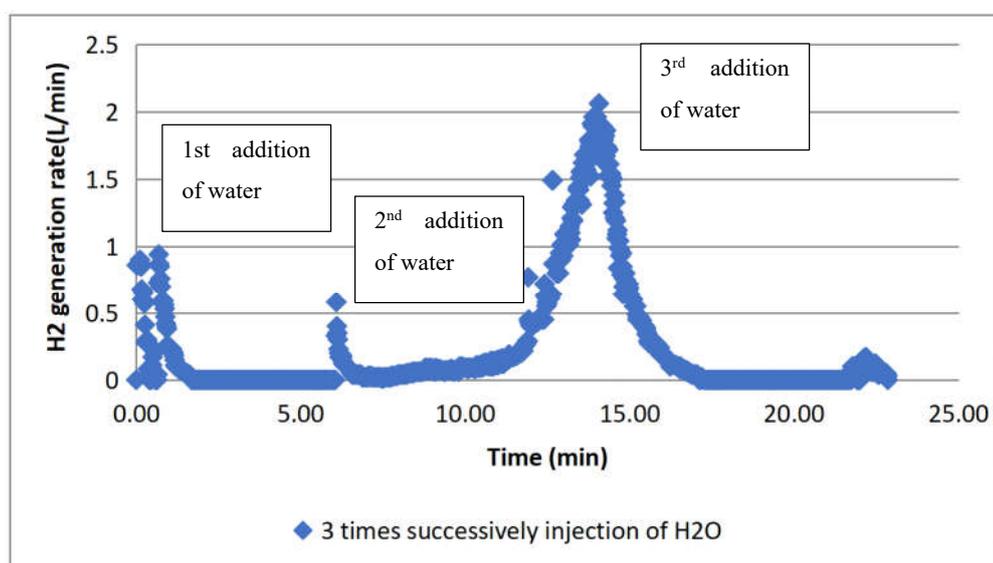


Figure 23 Variation of H₂ generation rate with time for 3 times successively injected H₂O (NaBH₄=5g, 1g FeCl₃ catalyst)

As can be seen from Figure 23, after 1st injection of stoichiometric amount of water, rate started to increase up to 1L/min. Then, it started to decrease until 6 minutes. At time, t=6 min, reaction finished and 2nd injection of H₂O was done. Immediately after the 2nd injection, H₂ generation rate started to increase to give a maximum rate of 0.58L/min. This reaction continued until 11 minutes. Finally, at t=11min, 3rd injection of H₂O was sent to the system and similar to the 2nd injection, rate started to increase to give a maximum rate of 2.06L/min. Reaction was finished at 23 minutes.

In Figure 24, the total amount of H₂ generated, when H₂O was introduced successively (R2-10) is compared with the same amount of water injected at the beginning of the reaction like in R2-9.

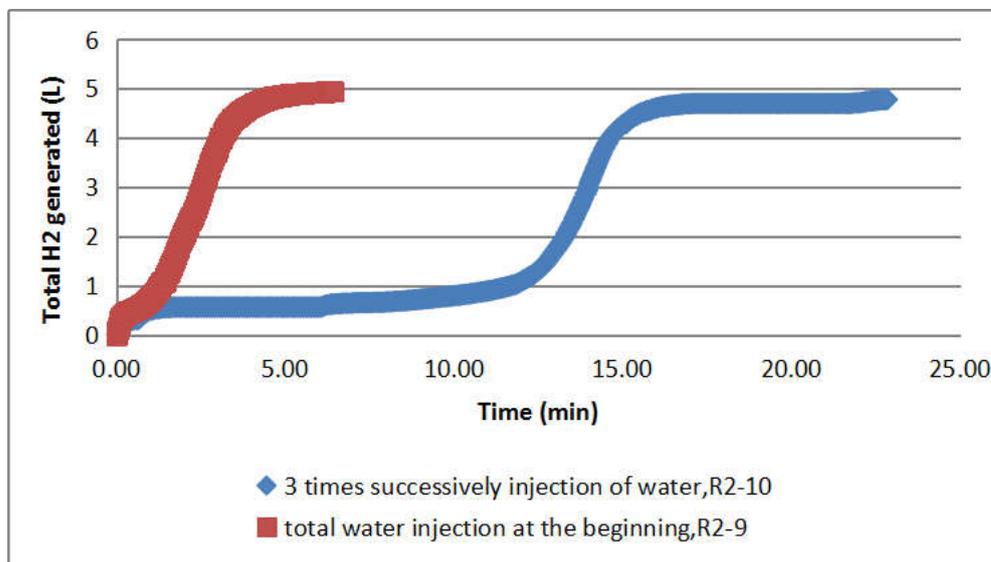


Figure 24 Total H₂ generated profile in different injection methods (NaBH₄=5g, 1g FeCl₃ catalyst, H₂O=14.3g)

For R2-10, H₂ generation efficiency and yield were calculated from Equations 5.1 and 5.2 as 37.0% and 1.0 respectively. For R2-9, H₂ generation efficiency and yield was found as 38% and 1.0 respectively. So, as shown in Figure 24, it can be concluded that supplying H₂O either at the beginning or successively has no dramatic effect on yield and efficiency. It affects the profile of H₂ generation rate. Furthermore, injecting the total amount of water at the beginning of the hydrolysis reaction is more practical. Besides, H₂ generation rate can be controlled by the water amount and injection method.

5.5 Effect of Reactor Geometry

In order to understand the effect of reactor geometry, 5g NaBH₄ and 0.5g solid FeCl₃ catalyst was placed into the various reactors. Stoichiometric amount of water which is 4.76g was injected into the reactor. Figure 25 shows the effect of reactor type on H₂ generation rate.

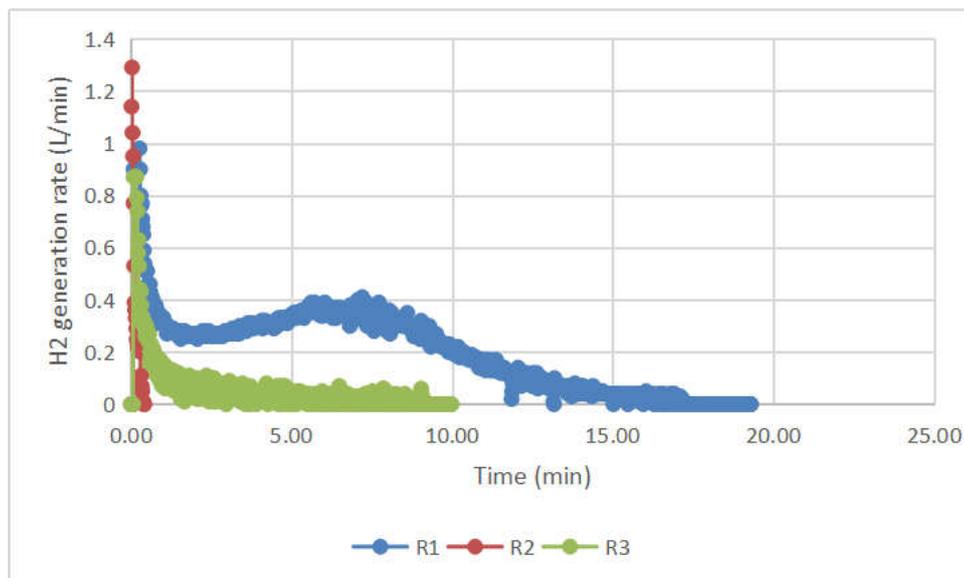


Figure 25 Effect of reactor type on H₂ generation flow rate (NaBH₄=5g, 4.76g H₂O, x=0, 0.5g solid FeCl₃ catalyst)

As shown in Figure 25, reactor type plays an important role on H₂ generation rate. Using large diameter of reactor like reactor 2 results lower rates of production. The dissolution of reactants may not so effective in large reactor diameters. Small diameters supply an effective mixing of reactants. Although Reactor 1 has small diameter and shows a good performance, its volume is not enough to meet high H₂ generation rate for large volume of reactants. So, Reactor 3 is chosen for further experiments.

5.6 Effect of hydration factor on H₂ generation rate in R3

5.6.1 Solid FeCl₃ catalyst

Effect of hydration factor on H₂ generation rate was investigated by the experiments R3-1 to R3-6. In all experiments, for start-up Case 1 as described in Chapter 4.1 was applied. 5g of NaBH₄ and 0.5g solid FeCl₃ were placed in R3. Then, desired amount of H₂O was injected directly into the R3. Figure 26 illustrates the effect of hydration factor on H₂ generation rate with respect to time.

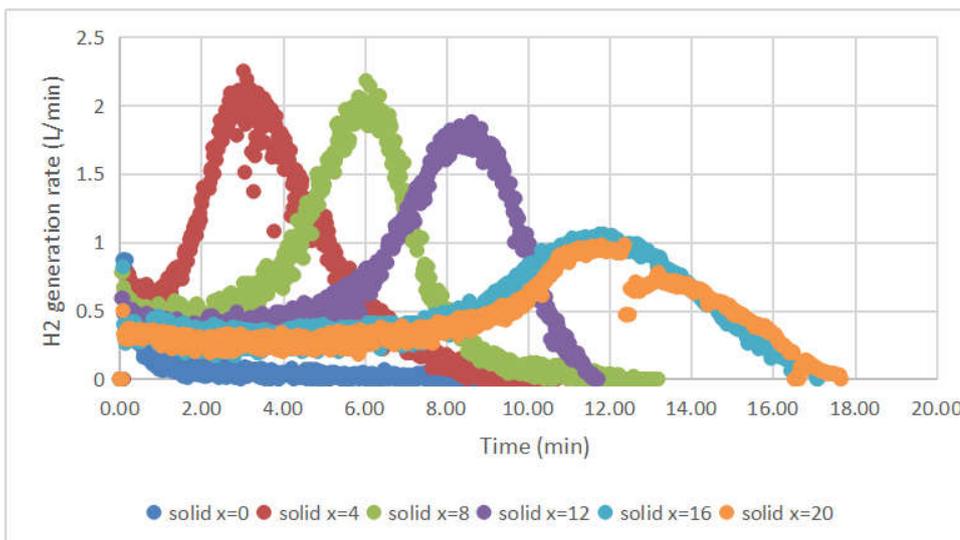


Figure 26 Variation of H₂ generation rate with time for different hydration factors (NaBH₄=5g, solid FeCl₃=0.5g)

As can be seen from Figure 26, H₂O has an important effect on H₂ generation rate and profile. As H₂O amount increases, the “reversed-V” shape shifts toward left. For further increase in water causes the rate profile became broader as like in R3-5 and R3-6 with x=16 and x=20. When stoichiometric amount of water was used, there was no maximum of H₂ generation rate occurred. Reaction rate continuously decreased for R3-1. For R3-2, maximum H₂ generation rate was obtained at t=3.2min as 2.12L/min. For R3-3, maximum H₂ generation rate was obtained at t=6.3min as 2.02L/min. For R3-4, maximum H₂ generation rate was obtained at t=8.6min as 1.88L/min. For both R3-5 and R3-6, maximum H₂ generation rate was obtained at t=12.2min as 1.03L/min.

Figure 27 shows the total H₂ generation rate with time for different hydration factors.

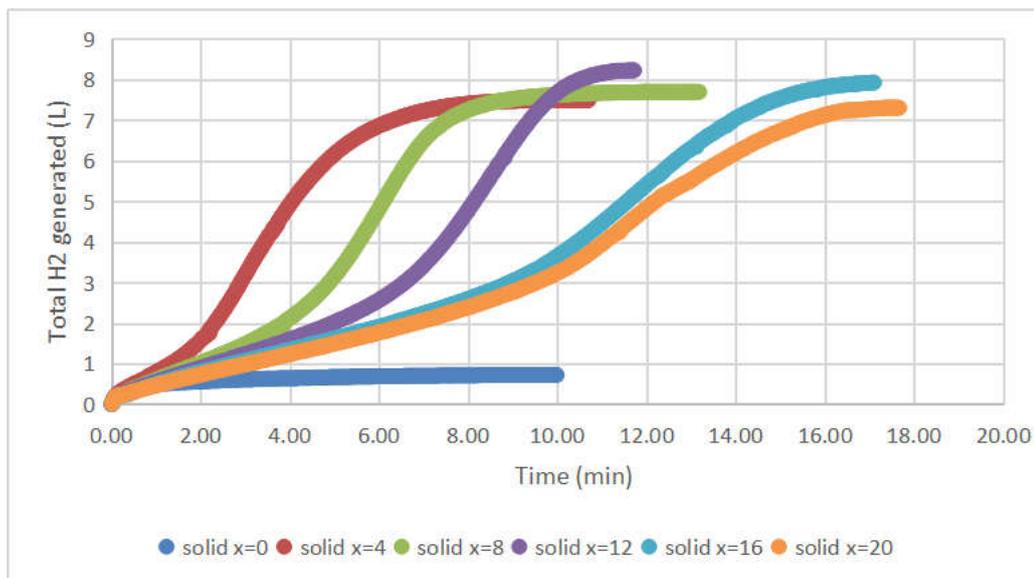


Figure 27 Total H₂ generation rate with time for different hydration factors (NaBH₄=5g, solid FeCl₃=0.5g)

From Figure 27, besides from R3-1 as stoichiometric amount of water was used, all experiments had total H₂ generated amount was higher than 7L.

Figure 28 shows the pictures of the reactor contents after each experiment.

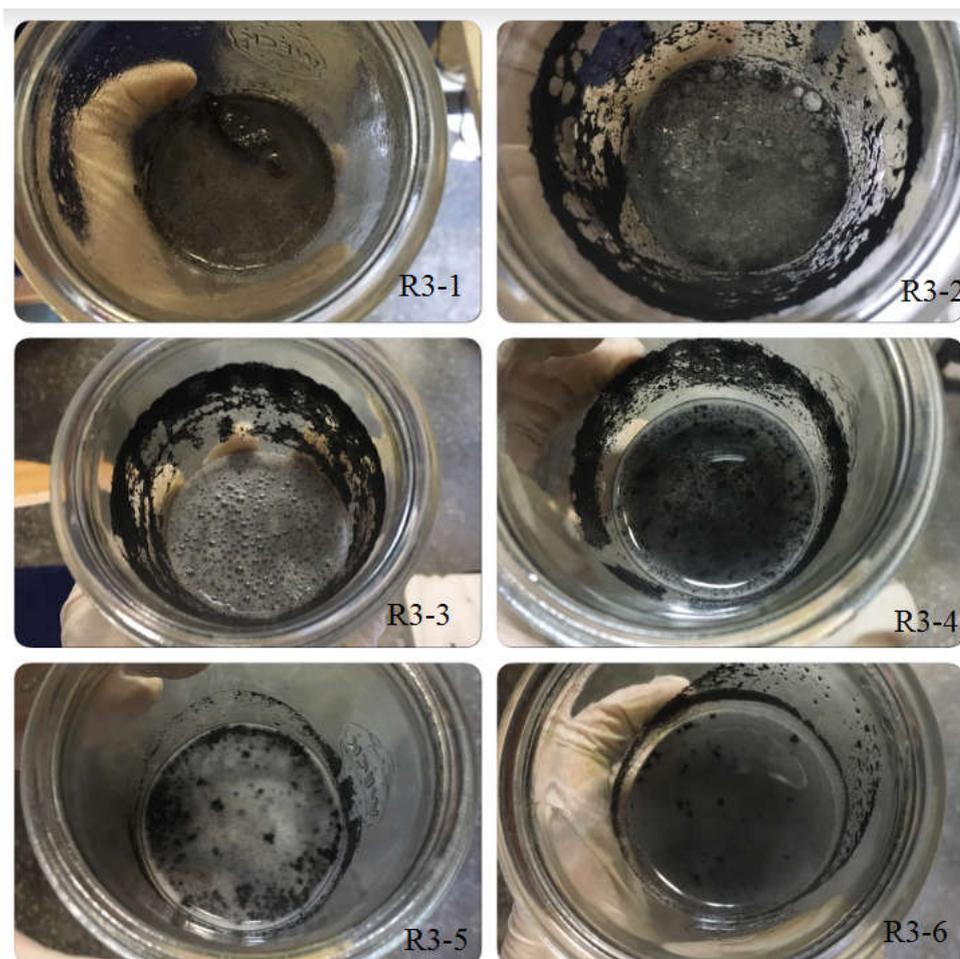


Figure 28 Picture of reactor contents after each experiment conducted with different hydration factors

Table 14 summarizes the results of the effect of hydration factor for solid 0.5g of FeCl_3 catalyst and 5 g of NaBH_4 .

Table 14 Results of the experiments conducted on Reactor 3 (R3) at different hydration factors, x (5g NaBH₄, 0.5g solid FeCl₃)

| Experiment Number | H ₂ O amount | Duration (min) | Mean H ₂ generation rate (L/min) | Total H ₂ Generated (L) | Yield (L H ₂ /g NaBH ₄) | Efficiency % |
|-------------------|-------------------------|----------------|---|------------------------------------|--|--------------|
| R3-1 | 4.8g, x=0 | 8.75 | 0.08 | 0.72 | 0.14 | 5.57 |
| R3-2 | 14.3g, x=4 | 7.77 | 0.95 | 7.49 | 1.50 | 57.94 |
| R3-3 | 23.8g, x=8 | 10.35 | 0.74 | 7.69 | 1.54 | 59.49 |
| R3-4 | 33.3g, x=12 | 11.53 | 0.71 | 8.22 | 1.64 | 63.59 |
| R3-5 | 42.8g, x=16 | 16.87 | 0.47 | 7.92 | 1.58 | 61.27 |
| R3-6 | 52.3g, x=20 | 17.38 | 0.42 | 7.30 | 1.46 | 56.47 |

From Table 14, as x increases up to 12, both H₂ generation yield and efficiency increases. For x>12, efficiency and yield decreases. It is concluded that optimization is definitely needed for water amount used in hydrolysis of NaBH₄. Also, from Figure 28, as H₂O amount increases, reactor contents stay in aqueous form, solidification of products was not observed at higher hydration factors.

5.6.2 Liquid (Aqueous) FeCl₃ catalyst

In order to investigate the effect of hydration factor on H₂ generation rate for aqueous FeCl₃ catalyst, Case 2 as explained in Chapter 4.1 was applied. This effect was investigated for two different experimental conditions. First set of

experiments conducted with 5g NaBH₄ and 0.5g FeCl₃ catalyst. Second set of experiments conducted with 10g NaBH₄ and 1g FeCl₃ catalyst.

In the first set of experiments, 5g of NaBH₄ was placed in R3. 0.5g solid FeCl₃ catalyst was dissolved in required amount of H₂O in order to obtain aqueous catalyst solution. Then, this solution was injected into the R3 to start H₂ generation. Figure 29 shows the variation of H₂ generation rate with time for different hydration factors.

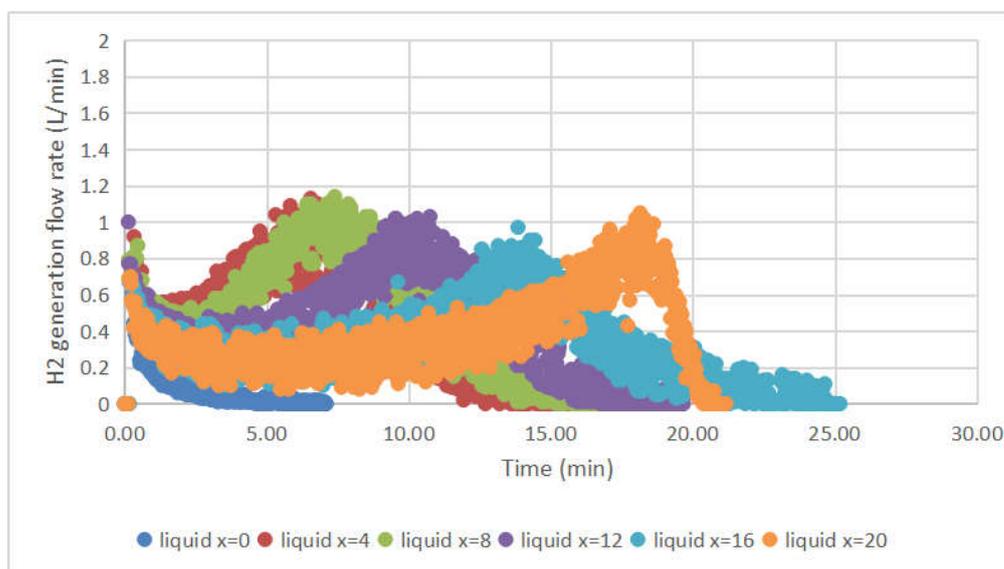


Figure 29 Effect of hydration factor on H₂ generation rate for aqueous 0.5g FeCl₃ catalyst (NaBH₄=5g)

From Figure 29, for R3-21, when x=0, “reversed-V” shape of profile was not observed. As H₂O increased to x=4, maximum H₂ generation rate was obtained as 1.13L/min at t=6.5min for R3-22. Maximum H₂ generation rate was obtained as 1.14L/min at t=7.4min for R3-23. For R3-24, maximum H₂ generation rate was obtained as 1.00L/min at t=10.6min. For R3-25, maximum H₂ generation rate was obtained as 0.86L/min at t=14min. Finally, for R3-26, maximum H₂ generation rate was obtained as 1.05L/min at t=18.2min. Different than others, in R3-26, immediately after the maximum H₂ generation rate was obtained, reaction was stopped at x=20. It did not show smooth decreasing behavior.

Figure 30 shows the total amount of H₂ generated with time for different hydration factors.

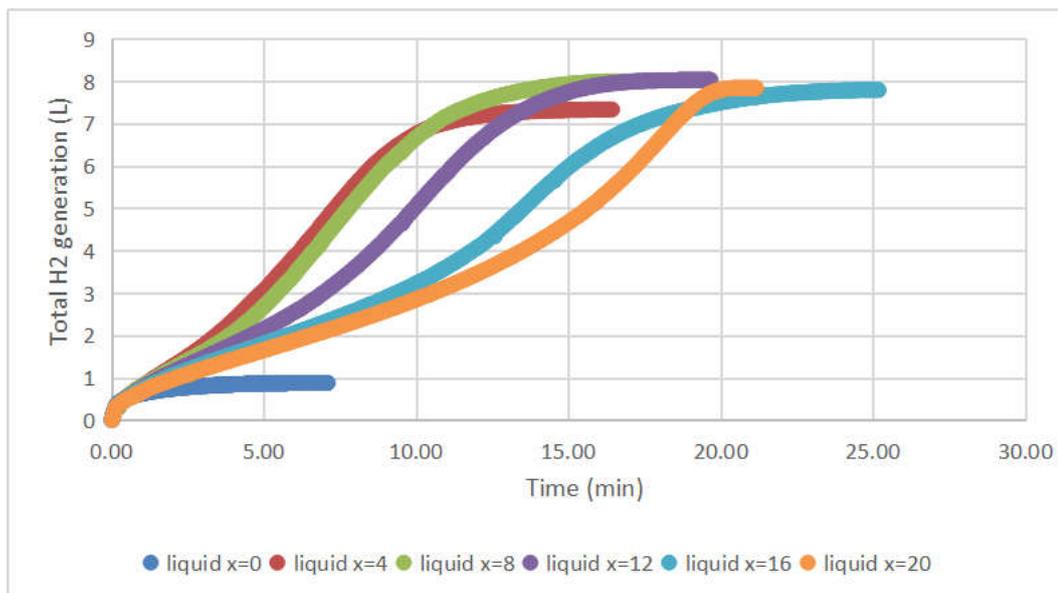


Figure 30 Total H₂ generated with time for different hydration factors for 0.5g FeCl₃ catalyst dissolved in H₂O (NaBH₄=5g)

As can be seen from Figure 27 and Figure 30, using Case 1 and Case 2 reached nearly same total H₂ generated amount. The difference is mean H₂ generation rate and duration. The reaction in Case 2 continued longer than in Case 1. Also mean H₂ generation rate obtained at Case 2 is higher than in Case 1.

Figure 31 shows the pictures of reactor contents after each reaction.



Figure 31 Pictures of reactor contents for different hydration factors. (5g NaBH_4 and 0.5g aqueous FeCl_3 catalyst)

As can be seen from Figure 31, when H_2O amount increases reactor contents stayed as dissolved in water. Solidification of the products was not observed at $x > 4$.

In the second set of experiments 10g of NaBH_4 was placed in R3. 1.0g solid FeCl_3 catalyst was dissolved in required amount of H_2O in order to obtain aqueous catalyst solution. Then, this solution was injected into the R3 to start H_2 generation. Figure 32 shows the variation of H_2 generation rate with time for different hydration factors.

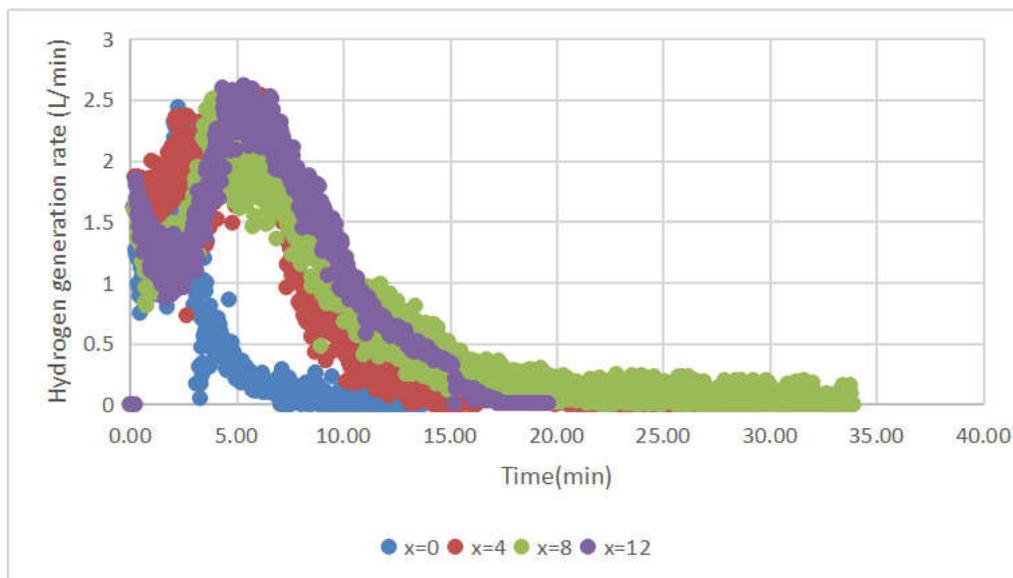


Figure 32 Variation of H₂ generation rate with time for 1.0 g FeCl₃ catalyst dissolved in H₂O (NaBH₄=10g)

As shown in Figure 32, all experiments included R3-27 when stoichiometric amount of H₂O was used, showed “reversed-V” shape of profile on H₂ generation rate. The maximum H₂ generation rate was obtained as 2.5L/min at t=2.3min for R3-27. For R3-28, the maximum H₂ generation rate was obtained as 2.5L/min at t=6.5min. For R3-29, the maximum H₂ generation rate was obtained as 2.54L/min at t=4min. Finally, for R3-30, the maximum H₂ generation rate was obtained as 2.6L/min at t=5.2min. Only for R3-30, when x=12, reaction continued until 35 minutes.

Figure 33 shows the variation of total H₂ generated with time for 10g NaBH₄ and 1.0 g aqueous FeCl₃ catalyst.

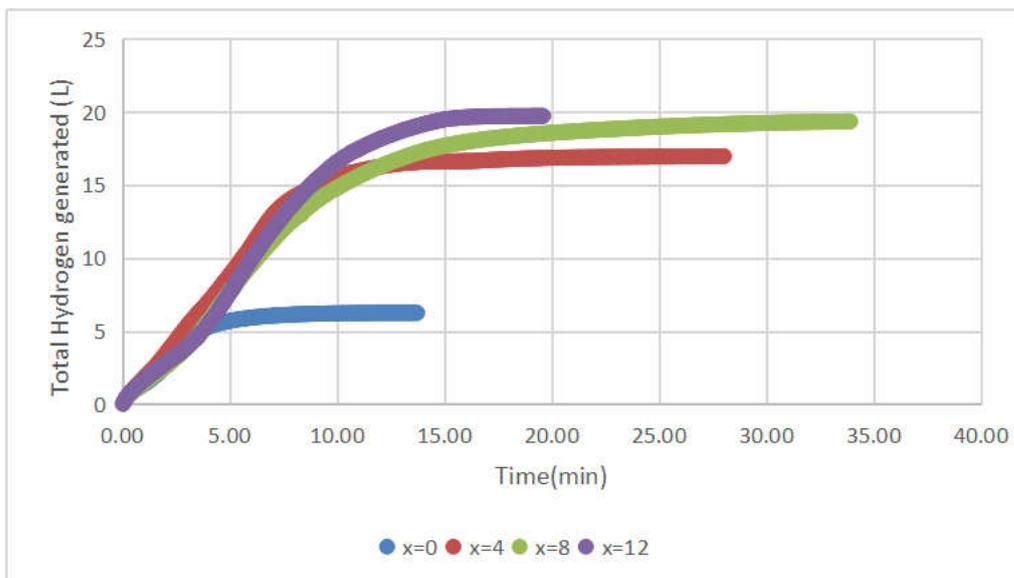


Figure 33 Total H₂ generated amount change with time for different hydration factors. (NaBH₄=10g, 1g FeCl₃ dissolved in desired amount of H₂O)

Figure 34 shows the pictures of reactor contents after each reaction.



Figure 34 Picture of the reactor contents after hydrolysis reaction finished

Table 15 summarizes the results of the experiments conducted for investigation of the effect of hydration factor on H₂ generation rate when FeCl₃ catalyst was used as in dissolved in water.

Table 15 Results of the experiments conducted on Reactor 3 (R3) at different hydration factors when FeCl₃ catalyst used in aqueous form.

| Experiment Number | NaBH ₄ amount (g) | H ₂ O amount | FeCl ₃ amount in liquid (g) | Total H ₂ Generated (L) | Duration (min) | Mean H ₂ generation rate (L/min) | Yield (L H ₂ /g NaBH ₄) | Efficiency % |
|-------------------|------------------------------|-------------------------|--|------------------------------------|----------------|---|--|--------------|
| R3-21 | 5.0 | 4.8g, x=0 | 0.5 | 0.88 | 3.10 | 0.26 | 0.18 | 6.81 |
| R3-22 | 5.0 | 14.3g, x=4 | 0.5 | 7.33 | 12.22 | 0.59 | 1.47 | 56.70 |
| R3-23 | 5.0 | 23.8g, x=8 | 0.5 | 8.00 | 14.15 | 0.55 | 1.60 | 61.89 |
| R3-24 | 5.0 | 33.3g, x=12 | 0.5 | 8.03 | 16.22 | 0.49 | 1.61 | 62.12 |
| R3-25 | 5.0 | 42.8g, x=16 | 0.5 | 7.79 | 22.12 | 0.35 | 1.56 | 60.26 |
| R3-26 | 5.0 | 52.3g, x=20 | 0.5 | 7.84 | 20.58 | 0.38 | 1.57 | 60.65 |
| R3-27 | 10.0 | 9.50g, x=0 | 1.0 | 6.25 | 5.12 | 1.11 | 0.63 | 24.17 |
| R3-28 | 10.0 | 28.5g, x=4 | 1.0 | 16.96 | 13.28 | 1.25 | 1.70 | 65.60 |
| R3-29 | 10.0 | 47.6g, x=8 | 1.0 | 19.34 | 17 | 1.07 | 1.93 | 74.81 |
| R3-30 | 10.0 | 66.6g, x=12 | 1.0 | 19.72 | 16.87 | 1.17 | 1.97 | 76.28 |

Table 15 shows the importance of water management in hydrolysis of NaBH_4 by using FeCl_3 catalyst as dissolved in water. The maximum efficiency and yield was obtained in R3-30 when 10g NaBH_4 was used at $x=12$ by dissolving 1.0g of FeCl_3 catalyst. These experimental conditions are promising to be tested in prototype reactor for fuel cell applications.

5.6.3 Solid CoCl_2 catalyst

Effect of hydration factor on H_2 generation rate was investigated on solid CoCl_2 catalyst in R3. For these experiments, for start-up, Case 1 was applied. 5g of NaBH_4 and 0.15g of solid CoCl_2 were placed in R3. Desired amount of water was injected into the reactor. Figure 35 shows the change of H_2 generation rate with time for different hydration factor.

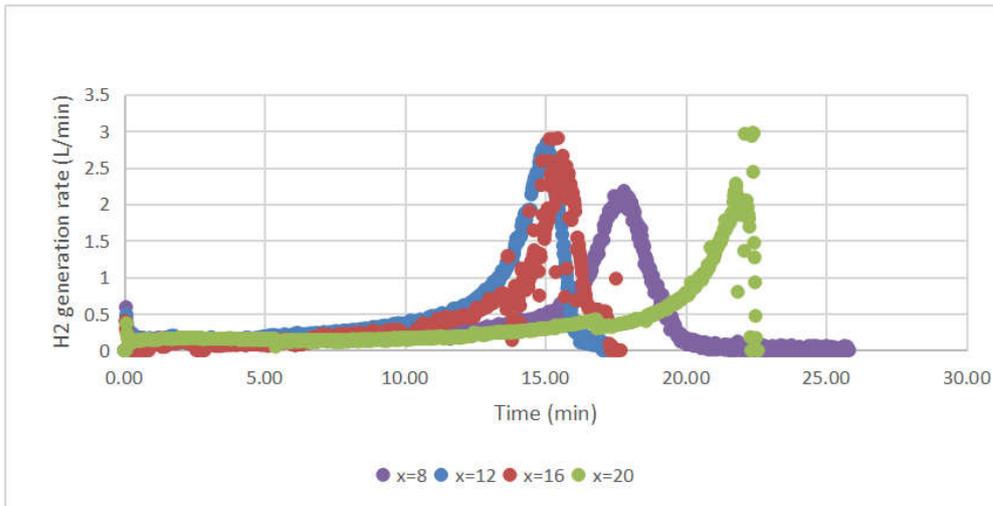


Figure 35 Variation of H_2 generation rate with time for different hydration factors ($\text{NaBH}_4=5\text{g}$, solid $\text{CoCl}_2=0.15\text{g}$)

From Figure 35, for R3-36 when $x=8$, reaction continued at a stable slow rate of approximately 0.2L/min for 15 minutes. Then, it gave a maximum rate of 2.1L/min at $t=18\text{min}$. For R3-37, when $x=12$, reaction continued stable rate of 0.3L/min for 10 minutes. Then, maximum H_2 generation rate was obtained at $t=15\text{min}$ as 2.8L/min. The maximum H_2 generation rate was obtained as 2.89L/min at $t=15.3$ for $x=16$. Finally for R3-39, when $x=20$, reaction continued

at a stable rate of 0.3L/min for 15 minutes, then the rate increased and the maximum H₂ generation rate was reached at t=22.3min as 2.98L/min, Reaction stopped immediately after reaching the maximum rate.

Figure 36 shows the total H₂ produced during these experiments.

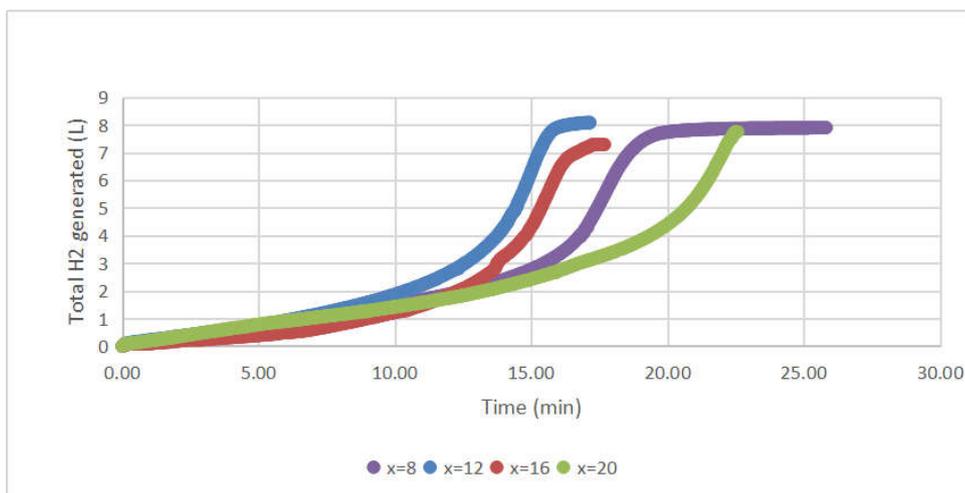
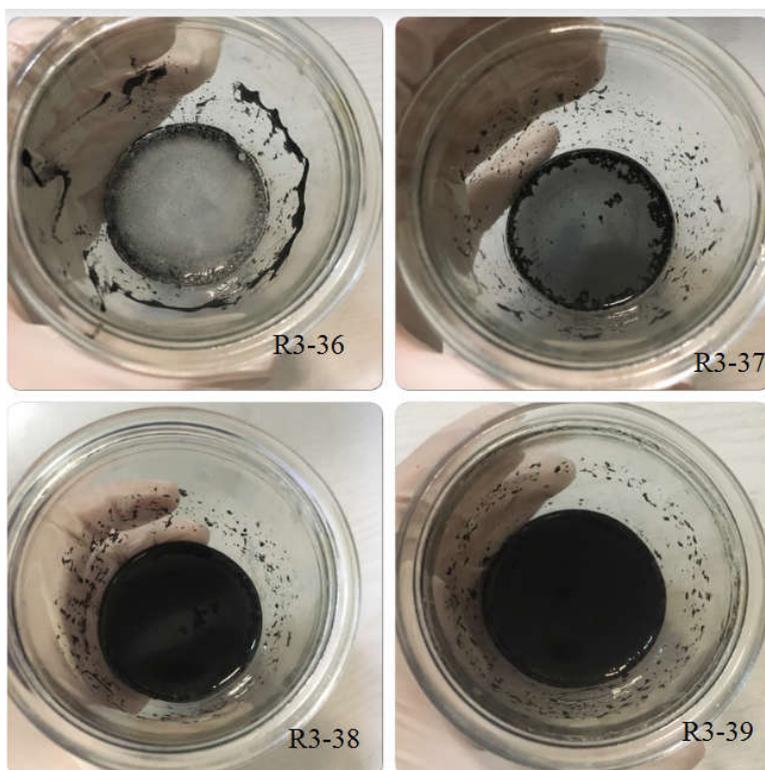


Figure 36 Variation of total H₂ generation with time for different hydration factors (NaBH₄=5g, solid CoCl₂=0.15g)

Figure 37(a) shows the pictures of reactor contents before the reaction and Figure 37(b) shows the pictures of reactor contents after each reaction.



(a)



(b)

Figure 37 (a) Picture of reactor contents before the reaction **(b)** Pictures of reactor contents after the reaction ceased.

Table 16 lists the results of the effect of hydration factor in R3 when 0.15g solid CoCl_2 catalyst was used.

Table 16 Results of the experiments conducted on Reactor 3 (R3) at different hydration factors for solid CoCl₂ (5g NaBH₄, 0.15g solid CoCl₂)

| Experiment Number | H ₂ O amount | Total H ₂ Generated (L) | Duration (min) | Mean H ₂ generation rate (L/min) | Yield (L H ₂ /g NaBH ₄) | Efficiency % |
|-------------------|-------------------------|------------------------------------|----------------|---|--|--------------|
| R3-36 | 23.8g, x=8 | 7.90 | 20.43 | 0.38 | 1.58 | 61.11 |
| R3-37 | 33.3g, x=12 | 8.08 | 16.17 | 0.48 | 1.62 | 62.52 |
| R3-38 | 42.8g, x=16 | 7.29 | 17.22 | 0.42 | 1.46 | 56.39 |
| R3-39 | 52.3g, x=20 | 7.75 | 22.57 | 0.34 | 1.55 | 59.95 |

From Figure 37, the color of the CoCl₂ catalyst was purple before the reaction. After the dissolution of CoCl₂ catalyst in water, Co⁺² undergoes a reduction and converts to Co⁺ according to Equation 3.7 as shown in Chapter 3. This causes the change in color of the catalyst from purple to black. Due to the dissolution of CoCl₂ catalyst in water, it undergoes reactions according to Equation 3.7 as shown in Chapter 3. This may cause a change in color of catalyst.

5.6.4 Liquid (Aqueous) CoCl₂ Catalyst

Effect of hydration factor was also investigated in R3 when CoCl₂ catalyst used as dissolved in H₂O. For these experiments as a start-up procedure Case-2 was applied. 5g of NaBH₄ was placed in R3. 0.15g CoCl₂ was dissolved in required amount of water to obtain catalyst solution. This catalyst solution was injected into the R3. Figure 38 illustrates the H₂ generation rate profile.

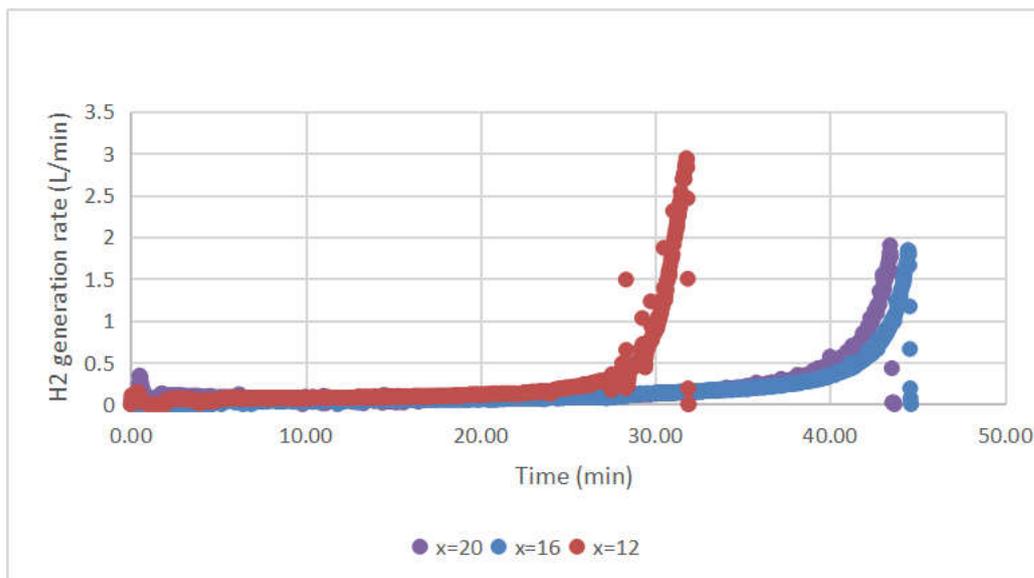


Figure 38 Variation of H₂ generation rate with time for various hydration factors. (NaBH₄=5g, aqueous CoCl₂=0.15g)

From Figure 38, in R3-48, when $x=12$, reaction continued for 28 minutes with a flow rate of 0.2L/min. At $t=32$ min, it gave its maximum generation rate of 2.98L/min and then it finished immediately. For R3-49 and for R3-50, reaction continued approximately 38 minutes with a flow rate of 0.2L/min. Maximum H₂ generation rate was found as 1.83L/min and 1.9 L/min for R3-49 and R3-50 respectively. For all of the experiments, reaction finished immediately after giving maximum H₂ generation rate. This behavior is decided to be not suitable for PEMFC applications because of the risk of sudden increase in hydrogen generation rate and thus increase in the solution volume suddenly which may damage the pipelines of reactor.

Figure 39 shows the variation of total H₂ amount with time for these three experiments.

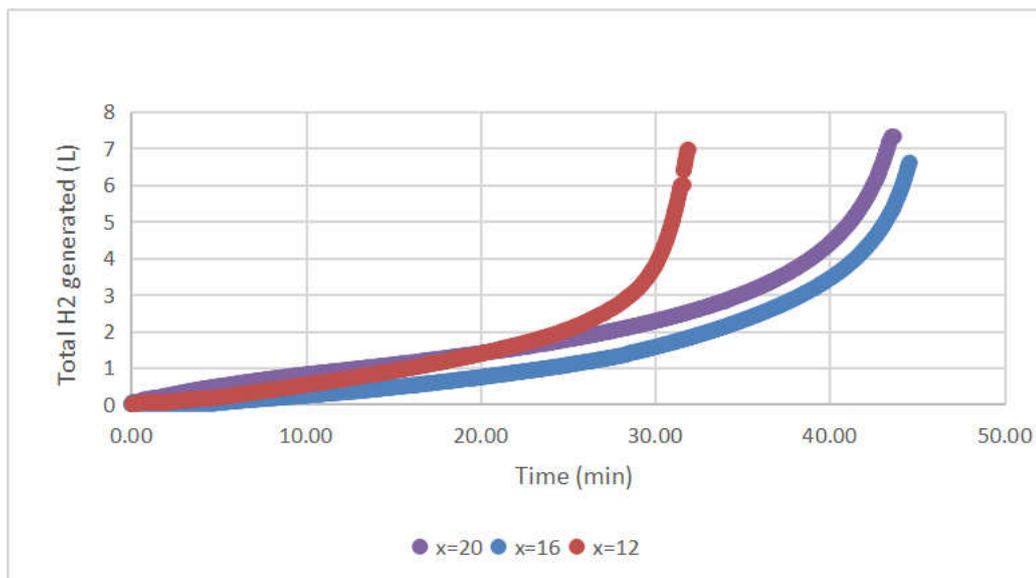


Figure 39 Total H₂ generated for various hydration factors when 0.15g CoCl₂ was dissolved in water. (NaBH₄=5g)

Figure 40 shows the pictures of reactor contents after each reaction finished.



Figure 40 Pictures of reactor contents after hydrolysis reaction

Table 17 summarizes the effect of hydration factor on H₂ generation rate when CoCl₂ catalyst was dissolved in water.

Table 17 Results of the experiments conducted on Reactor 3 (R3) at different hydration factors when CoCl₂ catalyst used in aqueous form (5g NaBH₄, 0.15g liquid CoCl₂)

| Experiment Number | H ₂ O amount | Total H ₂ Generated (L) | Duration (min) | Mean H ₂ generation rate (L/min) | Yield (L H ₂ /g NaBH ₄) | Efficiency % |
|-------------------|-------------------------|------------------------------------|----------------|---|--|--------------|
| R3-48 | 33.3g, x=12 | 6.95 | 31.82 | 0.22 | 1.39 | 53.76 |
| R3-49 | 42.8g, x=16 | 6.6 | 44.57 | 0.15 | 1.32 | 51.06 |
| R3-50 | 52.3g, x=20 | 7.31 | 43.67 | 0.17 | 1.46 | 56.55 |

For aqueous CoCl₂ experiments, in R3-48 efficiency value was calculated as 53.76%. When, x=16, efficiency value decreased to 51.06%. Further increase in hydration factor to x=20 results increase in efficiency. This behavior should be explained by the mechanism of the hydrolysis reaction under excess water.

Although, reaction continued for a very long time when compared to FeCl₃ catalyst and Case 1 for CoCl₂ catalyst, the mean H₂ generation rate for aqueous CoCl₂ catalyst was found to be lowest.

5.7 Effect of catalyst amount on H₂ generation rate in R3

5.7.1 Solid FeCl₃ catalyst

In order to see the effect of solid FeCl₃ amount on H₂ generation rate, Case 1 as discussed in Chapter 4.1 was applied for start-up procedure. 5g of NaBH₄ was placed in R3 together with desired amount of solid catalyst. 42.8g of H₂O (x=16)

was injected into the reactor for all of the experiments. Figure 41 shows the H₂ generation rate profile for various amounts of FeCl₃ catalyst. z

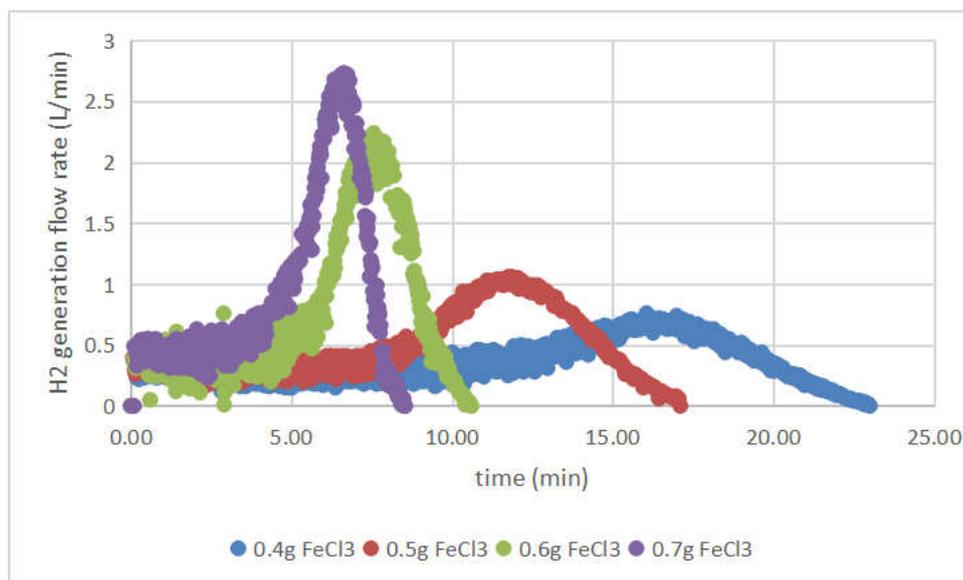


Figure 41 Variation of H₂ generation rate with time for different amount of solid FeCl₃ catalyst (NaBH₄=5g, H₂O=42.8g, x=16)

In Figure 41, H₂ generation rate increases as catalyst amount increases. When catalyst amount is higher or equal to 0.6g, H₂ generation rate profile will be narrower than using less amount of catalyst. When catalyst amount was decreased, reaction continued longer but with a slower H₂ generation flow rate. The maximum H₂ generation rate was obtained for R3-15, when 0.4g solid FeCl₃ was used, as 0.74L/min at t=17min. For R3-5, when 0.5g FeCl₃ was used, the maximum H₂ generation rate obtained as 1.06L/min at t=12min. For R3-16 (0.6g FeCl₃), the maximum H₂ generation rate was 2.24L/min at t=7.55min. For R3-17 (0.7g FeCl₃), the maximum H₂ generation rate occurred at t=6.8min with 2.67L/min.

Figure 42 illustrates the catalyst effect on total amount of H₂ generated.

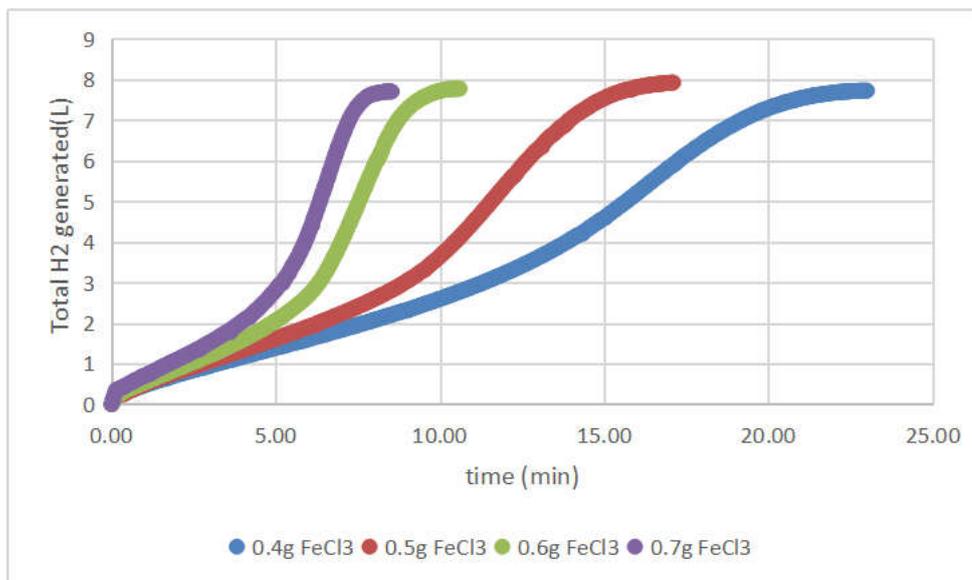


Figure 42 Total amount of H₂ generated with time for various amounts of solid FeCl₃ catalyst (NaBH₄=5g, H₂O=42.8g, x=16)

Table 18 shows the results of the solid FeCl₃ amount effect on H₂ generation rate.

Table 18 Results of the experiments conducted on Reactor 3 (R3) for different amounts of solid FeCl₃

| Experiment Number | NaBH ₄ amount (g) | H ₂ O amount | Solid FeCl ₃ amount (g) | Total H ₂ Generated (L) | Yield (L H ₂ /g NaBH ₄) | Efficiency % |
|-------------------|------------------------------|-------------------------|------------------------------------|------------------------------------|--|--------------|
| R3-15 | 5.0 | 42.8g, x=16 | 0.4 | 7.72 | 1.54 | 59.72 |
| R3-5 | 5.0 | 42.8g, x=16 | 0.5 | 7.92 | 1.58 | 61.27 |
| R3-16 | 5.0 | 42.8g, x=16 | 0.6 | 7.77 | 1.55 | 60.11 |
| R3-17 | 5.0 | 42.8g, x=16 | 0.7 | 7.70 | 1.54 | 59.57 |

From Table 18 and Figure 42, as catalyst amount increases, the efficiency of the hydrolysis reaction does not change too much. The reaction profile can be controlled by catalyst amount in excess water. In Reactor 1, it was seen that efficiency values increase with increasing catalyst amount. But, in R1, this effect was investigated on stoichiometric amount of water. So, for excess water, solid FeCl₃ amount affects only the rate behavior.

5.7.2 Liquid (aqueous) FeCl₃ catalyst

The effect of aqueous FeCl₃ amount on H₂ generation rate was analyzed for Case 2. 10g of NaBH₄ was placed in R3. Two sets of experiments was conducted in order to investigate this effect.

In the first set of experiment, 0.5g FeCl₃ for R3-31, 0.7g FeCl₃ for R3-32 and for R3-30, 1.0g FeCl₃ was dissolved in 66.6g of H₂O (x=12). This catalyst solution was injected into the reactor for all of the experiments. Figure 43 shows the H₂ generation rate profile for various amounts of liquid FeCl₃ catalyst.

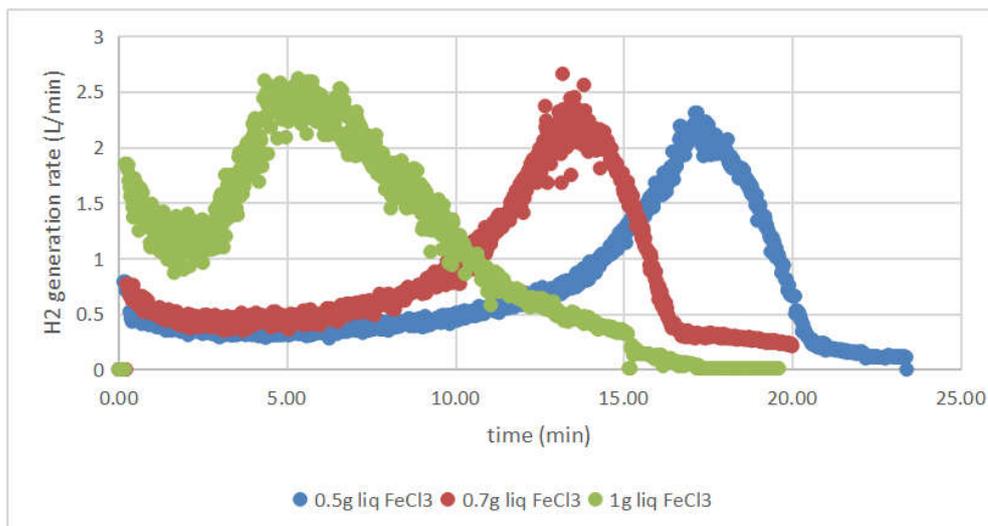


Figure 43 Variation of H₂ generation rate with time for various amounts of liquid catalyst (NaBH₄=10g, H₂O=66.6g, x=12)

From Figure 43, maximum H₂ generation rates was found as 2.24L/min, 2.45L/min and 2.62L/min for 0.5g, 0.6g and 0.7g FeCl₃ catalyst was dissolved in 66.6g H₂O respectively. As catalyst amount in water increases, rate increases but, rate profile narrowed.

Figure 44 shows the total H₂ generated with time.

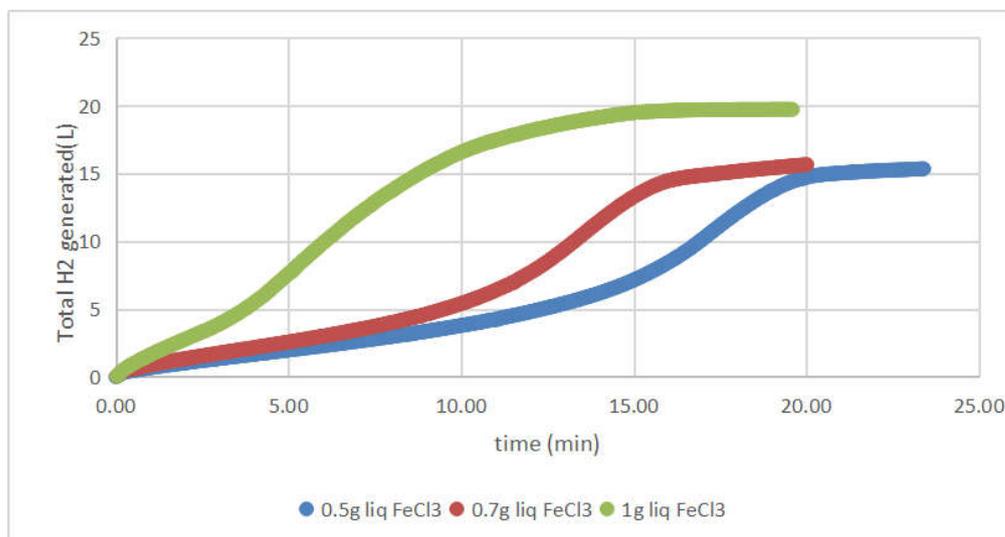


Figure 44 Variation of total H₂ generated with time (NaBH₄=10g, H₂O=66.6g, x=12)

As FeCl_3 amount dissolved in excess H_2O increases, the H_2 generation efficiency increases too. In Case 1, when solid catalyst was used, the efficiency was found to be nearly same for all catalyst amounts as discussed in Chapter 5.6.1. For Case 2, the catalyst in water amount changed, it changes the efficiency. This phenomena can be explained by different mechanism applied for Case 1 and Case 2.

In the second set of experiment, 0.3g FeCl_3 for R3-33, 1.0g FeCl_3 for R3-34 and for R3-35, 6.0g FeCl_3 was dissolved in 9.5g of H_2O ($x=0$). This catalyst solution was injected into the reactor for all of the experiments. Figure 45 shows the H_2 generation rate profile for various amounts of liquid FeCl_3 catalyst.

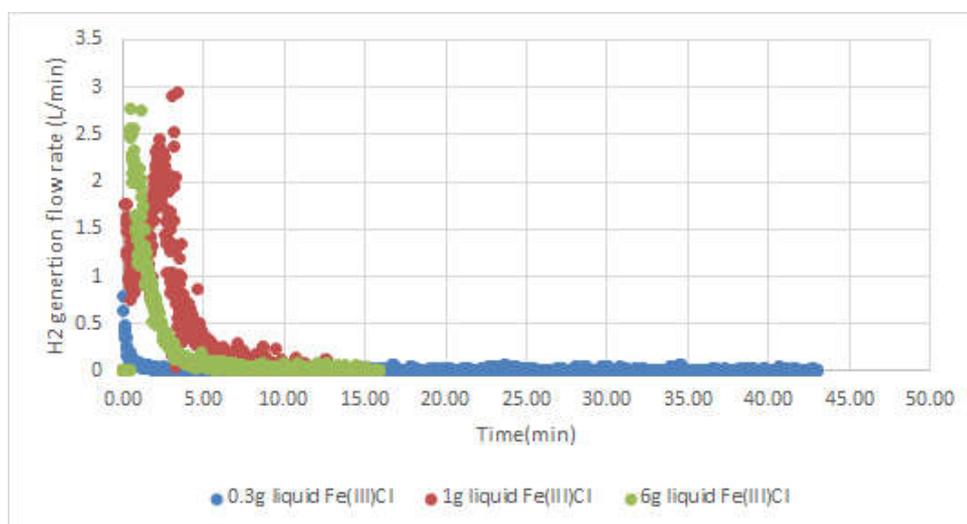


Figure 45 H_2 generation rate profile on stoichiometric amount of water (10g NaBH_4 , 9.5g H_2O , $x=0$)

Figure 46 shows the total H_2 produced with time for each experiment.

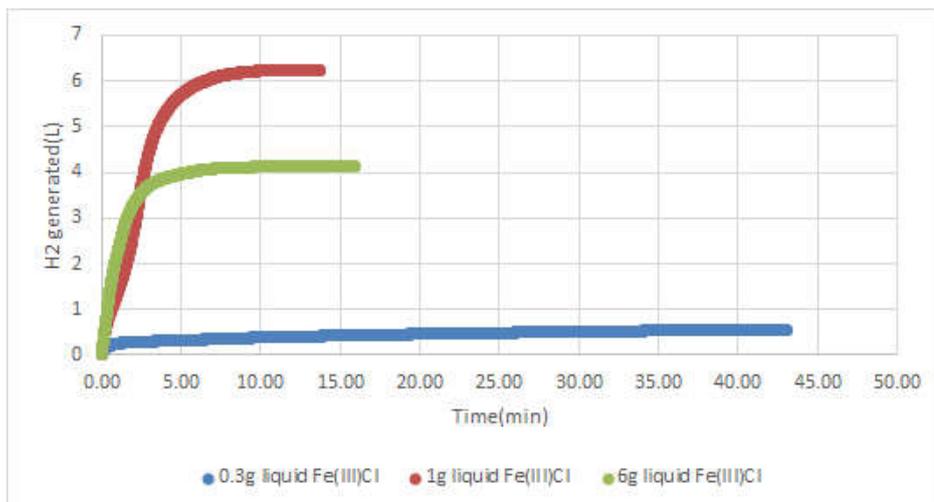


Figure 46 Change of total H₂ generated with time (10g NaBH₄, 9.5g H₂O, x=0)

Table 19 summarizes the results of each experiment conducted with liquid FeCl₃ catalyst solution.

Table 19 Results of the experiments conducted on Reactor 3 (R3) for different amounts of solid FeCl₃

| Experiment Number | NaBH ₄ amount (g) | H ₂ O amount | FeCl ₃ amount in liquid (g) | Total H ₂ Generated (L) | Yield (L H ₂ /g NaBH ₄) | Efficiency % |
|-------------------|------------------------------|-------------------------|--|------------------------------------|--|--------------|
| R3-31 | 10.0 | 66.6g, x=12 | 0.5 | 15.34 | 1.53 | 59.33 |
| R3-32 | 10.0 | 66.6g, x=12 | 0.7 | 15.65 | 1.57 | 60.53 |
| R3-30 | 10.0 | 66.6g, x=12 | 1.0 | 19.72 | 1.297 | 76.27 |
| R3-33 | 10.0 | 9.5g, x=0 | 0.3 | 0.57 | 0.06 | 2.20 |
| R3-34 | 10.0 | 9.5g, x=0 | 1.0 | 6.25 | 0.63 | 24.17 |
| R3-35 | 10.0 | 9.5g, x=0 | 6.0 | 4.14 | 0.41 | 16.01 |

When the catalyst amount was increased from 0.3g to 1g FeCl₃ in stoichiometric amount of water, total hydrogen generation and efficiency increased up to 6.25L and 24.17% respectively. However, further increase to of the catalyst to 6g FeCl₃ catalyst, it was observed that, water immediately reacted with the small portion of NaBH₄ as soon as it contacted and formed solid byproducts. The remaining NaBH₄ could not access water and therefore left unreacted. Thus, in this case hydrogen generation and efficiency were dropped to 4.14 L and 16 %.

5.8 Effect of water type on H₂ generation rate in R3

Effect of water type in R3 was investigated by using 3 types of water; bottled drinking water, tap water and 2μs ultra-pure de-ionized water. For these experiments, Case 1 was applied for start-up. 5g NaBH₄ and 0.5g solid FeCl₃ was

placed in the reactor. 33.3g (x=12) of water with different types was injected into the reactor. Figure 47 shows this effect on H₂ generation rate profile

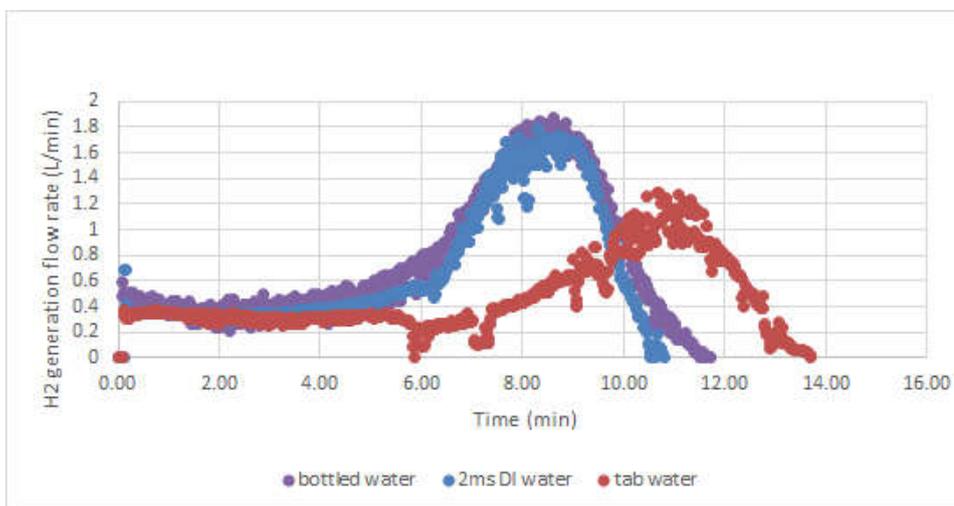


Figure 47 Effect of water type on H₂ generation rate (5g NaBH₄, 33.3g H₂O, x=12, 0.5g solid FeCl₃)

From Figure 47, it is concluded that using either ultra-pure de-ionized water or bottled water does not affect H₂ generation rate. However, for tap water, the rate was found to be less than using bottled or de-ionized water. Impurities in tap water may block the catalyst and cause decrease in H₂ generation rate. So, tap water use in hydrolysis of NaBH₄ is not recommended.

5.9 XRD Results of Catalysts

Throughout the experimental study, FeCl₃ catalysts turned from yellow to black color whereas, CoCl₂ catalyst turned purple to black color during the hydrolysis of NaBH₄. In order for better understanding the mechanism behind this color change XRD samples of the catalysts were taken. Figure 48 shows the XRD result of FeCl₃ before the reaction and Figure 49 shows the XRD result of FeCl₃ catalyst after the hydrolysis reaction.

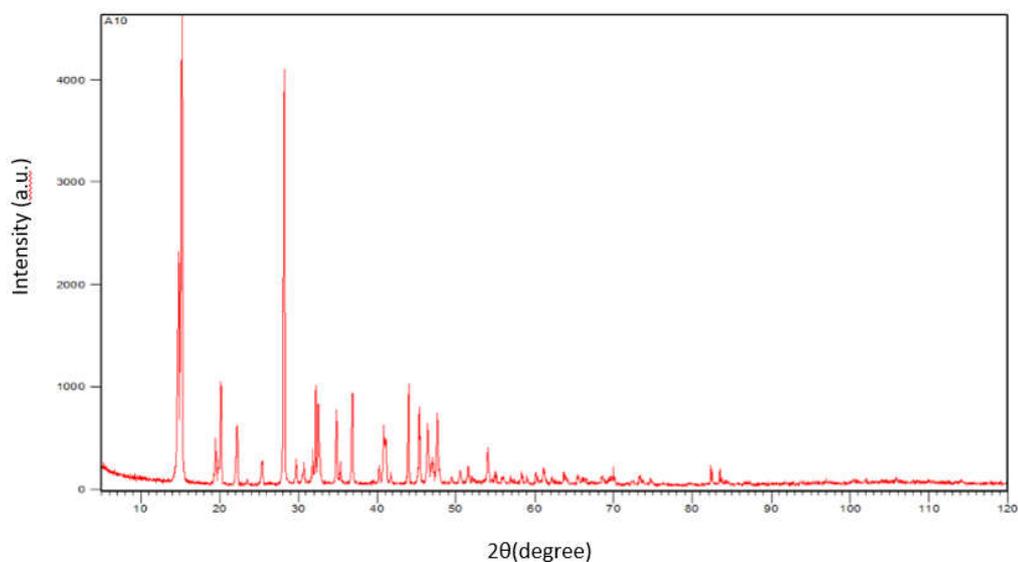


Figure 48 XRD result of FeCl_3 catalyst before the hydrolysis reaction

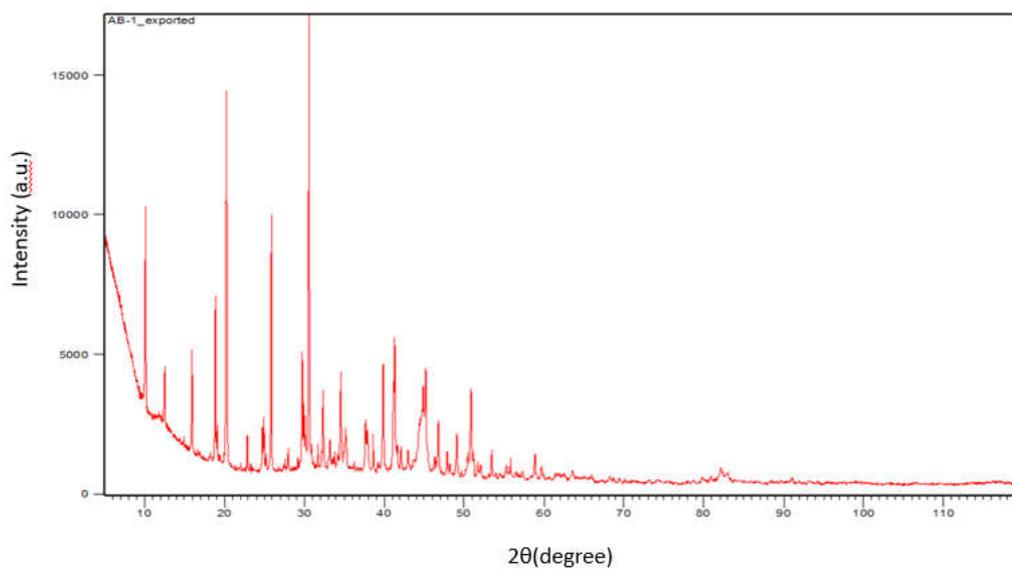


Figure 49 XRD result of FeCl_3 catalyst after the hydrolysis reaction

From the XRD patterns, it can be interpreted that some peaks of FeCl_3 after the reaction is same with the pure one. However, most intense peaks did not match with each other. Further analysis shows that some peaks of FeCl_3 recovered after the reaction belong to Fe(s) and Fe_2O_3 . This can be interpreted from Figure 50.

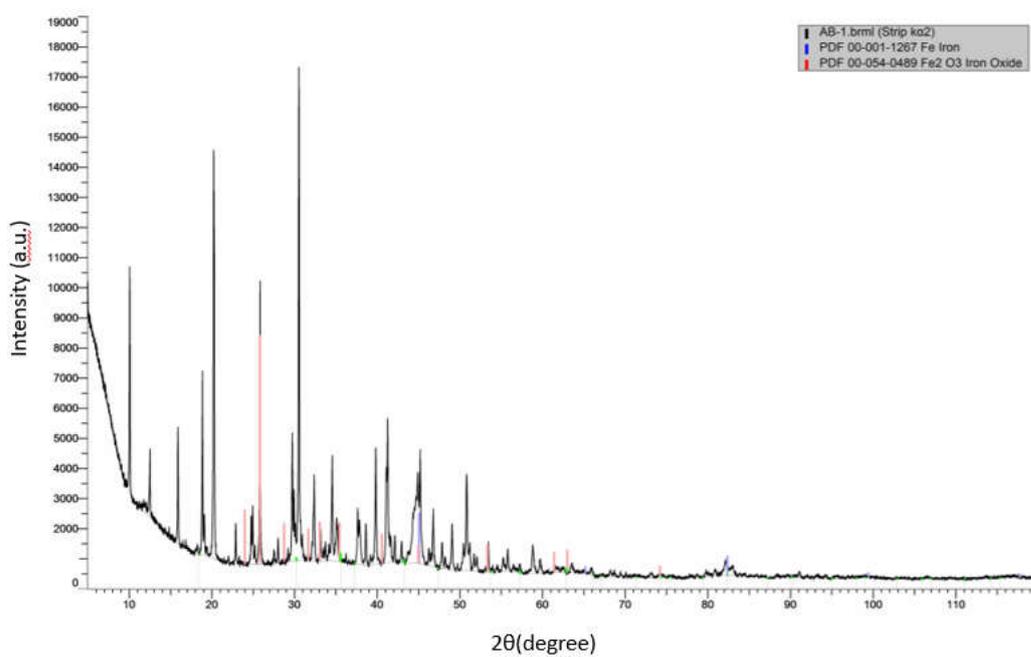


Figure 50 Fe and Fe₂O₃ XRD peaks matched for FeCl₃ catalyst after the reaction

Figure 51 shows the XRD pattern of CoCl₂ catalyst before the reaction whereas, Figure 52 shows the XRD result of CoCl₂ catalyst after the reaction.

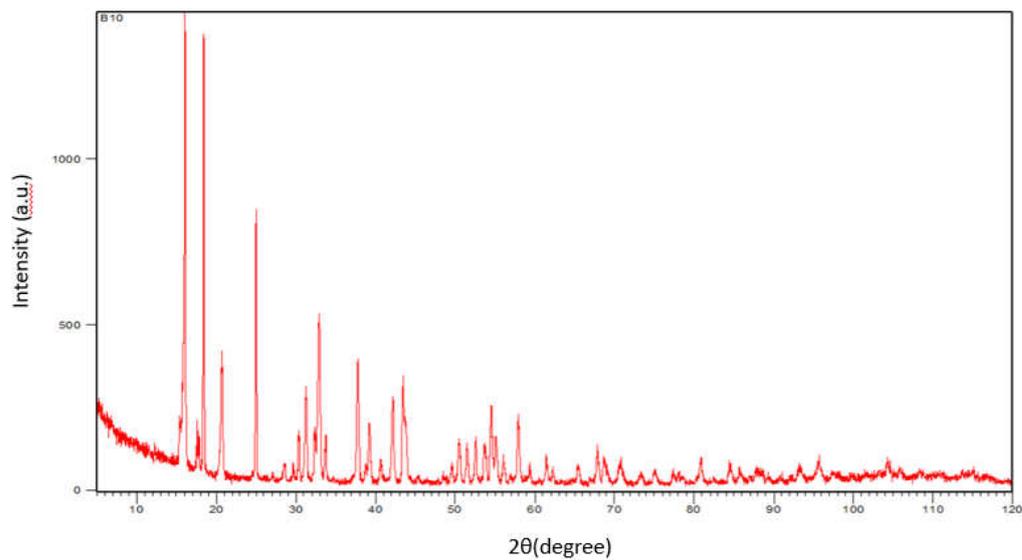


Figure 51 XRD result of CoCl₂ catalyst before the hydrolysis reaction

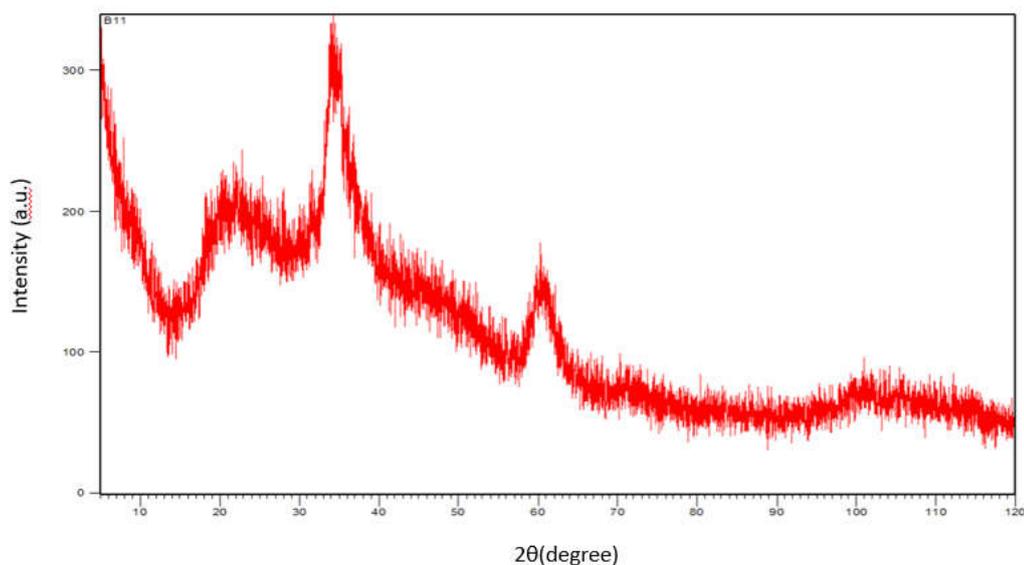


Figure 52 XRD result of CoCl_2 catalyst after the hydrolysis reaction

From the Figure 51 and 52, the phase of CoCl_2 catalyst before the reaction and the phase of CoCl_2 were not the same. Further analysis is recommended for determining the consisted phases.

Although the formation of black precipitate was composed of few compounds that are Co precursor such as CoCl_2 and NaBH_4 , identification of this black solid is not easy [86]. Demirci et al. [86] investigated Co-based catalyzed NaBH_4 hydrolysis. They followed a systematic approach and discussed characterization methods like ICP-AES, XRD, and XPS in order to identify the black solid remaining after the hydrolysis reaction of NaBH_4 . They also emphasized different literature findings regarding to the black solid. It is evident that NaBH_4 has the ability to reduce any Co precursor (mainly CoCl_2) and forms black precipitate. In literature, it is more commonly believed that, this black precipitate is Co_xB or Co-B [86].

5.10 Evaluation of Kinetic Experiments

Kinetic experiments were conducted in three different reactor geometries in order to see the effect of reactor geometry on hydrogen generation rate. Reactor size and geometry plays an important role in H₂ generation rate and efficiency. Reactor with small diameter has better performance as it enables the reactants to mix more efficiently. So, Reactor 3 was chosen as optimum reactor in terms of performance for fuel cell tests.

It has been concluded from conducted kinetic experiments that H₂ generation rate was very slow when catalyst was not used. So, catalyst is necessary to meet the PEMFC requirements.

Hydration factor is found to be one of the most critical parameter for solid state NaBH₄ hydrolysis reaction. When stoichiometric amount of water was used, H₂ generation occurs at a very slow rate and efficiency. So, excess water is needed for solid state H₂ generation from NaBH₄. Excess water also enables the products to stay at their aqueous forms. At higher hydration factors $x > 4$, precipitation of sodium metaborate did not occur. Therefore, water amount is optimized according to the H₂ generation yield.

For the usage method of catalyst in hydrolysis reactor, two different cases were investigated: In Case 1, solid catalyst (either FeCl₃ or CoCl₂) was mixed with solid NaBH₄ in the reactor. Then, water was injected into the reactor to initiate hydrolysis reaction. In Case 2, solid catalyst (either FeCl₃ or CoCl₂) was dissolved in water. Then, catalyst solution was injected into the reactor that contains only solid NaBH₄ to initiate the H₂ generation. Both cases were found to be appropriate for fuel cell tests. Actually, the method of the use of catalyst must be determined by considering practical applications.

Although CoCl₂ catalyst showed good activity, the behavior of releasing hydrogen is not appropriate for fuel cell tests. It showed very low hydrogen generation rate with long period of time and then followed by sudden increase in hydrogen generation rate. It is not suitable for on demand applications since it requires a

lack time to generate the desired amount of hydrogen. Also, sudden increase in rate may cause a damage of pipelines of reactor.

The maximum H₂ generation efficiency obtained at 10g NaBH₄ at x=12 when 1.0g of FeCl₃ catalyst was dissolved in water as 76.28% as for Case 2. This condition is found to be promising for fuel cell integration.

Kinetic experiments were repeated three times and found to be reproducible.

The effect of water type was also investigated. The experiments conducted with de-ionized water and 2μs conductivity ultra-pure water hydrolysis resulted similarly. However, tap water use in hydrolysis of NaBH₄ as reactant is not recommended due to its content of impurities which results in lower production rate.

CHAPTER 6

INTEGRATION OF DEVELOPED SOLID NaBH₄ SYSTEM WITH PEMFC

As a result of kinetic experiments the maximum H₂ generation efficiency (76.28%) is obtained with 10g NaBH₄, hydration factor of $x=12$ when 1.0g of FeCl₃ catalyst was dissolved in water and injected to Reactor 3. This condition is found to be promising to be tested in prototype reactor for fuel cell applications. CoCl₂ catalyst was not selected because of the reasons that were explained in previous chapter. There are a lot of kinetic studies conducted on cobalt based catalysts as given in Chapter 2, CoCl₂ catalyst requires a long activation time. Besides, H₂ is generated in a very short time at a very high rate. This is therefore not suitable for a PEMFC. PEMFC requires supplying H₂ in a longer period of time at a steadier rate. In Chapter 5, it has been proven that FeCl₃ catalyst activate very fast and H₂ gas evolve for a prolong time which is suitable for fuel cell applications. The overall yield is almost the same for both catalysts which is also acceptable.

In order to achieve the goal of this Ph.D thesis, the developed solid NaBH₄ hydrolysis system is integrated to a PEMFC to generate electricity for portable applications. The performance of the integrated system is recorded by a test station.

6.1 First integration with PEMFC

Sodium borohydride hydrolysis reactor was connected to anode side of a one cell PEMFC which has membrane electrode assembly (MEA1) previously prepared by Dr. Serdar Erkan. [79]

Fuel cell has an active area of 10cm^2 and with a maximum power of 60W .

The picture of PEMFC is shown in Figure 53.

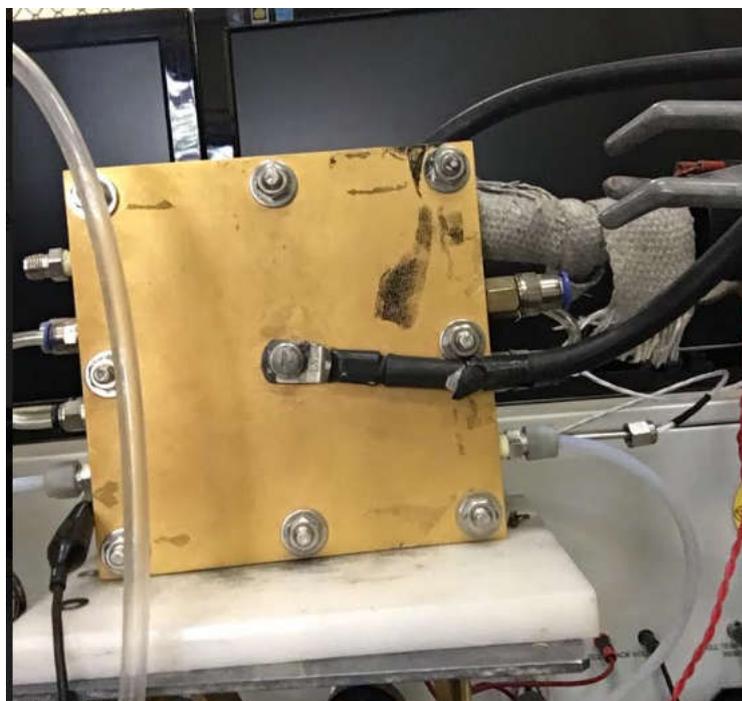


Figure 53 Picture of PEMFC.

Figure 54 shows the integrated PEMFC system with NaBH_4 hydrolysis reactor.



Figure 54 Integrated NaBH_4 hydrolysis reactor with one cell PEMFC

First set of fuel cell test experiments was planned to be 3 successive tests with same amount of NaBH_4 , water and catalyst. For these tests 10g of NaBH_4 was placed in Reactor 3. 1.0g of FeCl_3 catalyst was dissolved in 66.6g water ($x=12$) and then injected to the reactor in order to start H_2 generation. The oxygen flow rate was constant at 0.9L/min. The cell voltage was kept constant at 0.5V. The cell voltage, current and cell temperature were recorded online for every 1 min.

For further testing of developed NaBH_4 system in PEMFC, a new membrane electrode assembly (MEA2) is manufactured. In the following Section 6.2, the preparation method for MEA is explained in detail.

6.2 Preparation method of MEA's for PEM fuel cell

MEA is the heart of fuel cell system which composed of two catalyst layers for both anode and cathode side of fuel cell. For the preparation of MEA's first catalyst ink solution was prepared and then coated on gas diffusion layer (GDL) by using SONOTEK Exacta Coat equipment. This technique had been applied was previously developed in METU FCRC group and called "spraying of catalyst ink with air pressure atomizing spray gun". [79] Figure 55 shows the picture of this equipment.



Figure 55 SONOTEK Exacta Coat Equipment

For catalyst ink preparation, 47.7% Pt load TANAKA catalyst (lot no: 109H-0181), Nafion® solution (Liquion™ Ion Power®) and GDLs (GDL 30 BC) from

SGL Carbon (Germany) was used. The platinum loading was set to 0.4 mgPt/cm², whereas Nafion® loading was set to 30wt% dry basis in catalyst ink. The catalyst ink was sprayed until the desired catalyst loading (0.4 mgPt/cm²) for both anode and cathode sides) was achieved. Moreover, as a membrane Nafion® 212 which has a 50 micron thickness was used.

First 10x10cm GDL's were prepared. 0.2096g of catalyst was weighted and putted in a glass flask. 2mL of de-ionized water added on the catalyst. Then, 0.6g of 15wt% Nafion® solution was added. Finally total volume of catalyst ink solution was completed to 84 mL with 1:7 ratio of water to 2-propanol. When catalyst ink was prepared, it was allowed to mix in ultrasonic stirrer for 20 minutes before coating. For spray coating of GDL's the feed rate of solution was set to 0.6mL/min. Spray head speed was 20mm/sec and frequency of 48kHz. 5 seconds was left in each cycle of spraying to allow drying the catalyst layer. After the catalyst layers were prepared, they pressed on to the Nafion® 212 membrane at 130°C, 250 psi for 3 minutes. Finally the MEA's were ready to be used in PEM fuel cell.

For performance tests with new prepared MEA's, the fuel cell voltage was kept constant at 0.55V and air flow rate of 0.56 L/min for all experiments.

6.3 Results of Experiments Conducted with PEMFC

6.3.1 Results of the first fuel cell integration

As explained in Section 6.2, for fuel cell experiments, 10g NaBH₄ at x=12 when 1.0g of FeCl₃ catalyst was dissolved in water as 76.28% in Reactor 3 was selected to be used. For this condition, H₂ generation rate was shown in Figure 56.

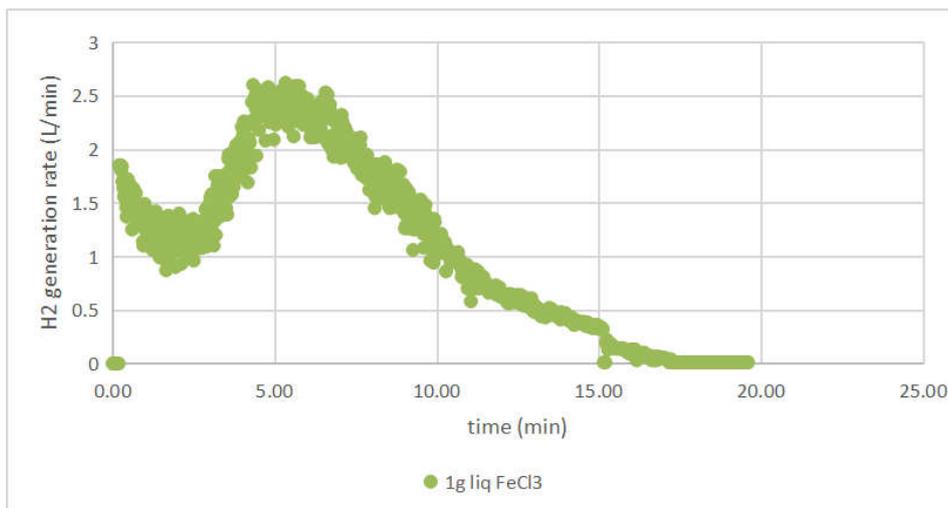


Figure 56 Variation of H₂ generation rate with respect to time

After first test, fresh NaBH₄ was placed in the reactor. Again fresh catalyst solution was prepared and injected into the reactor for second test. These conditions were applied for all 3 successive fuel cell tests.

Figure 57 illustrate the performance of the fuel cell integration with NaBH₄ hydrolysis reactor.

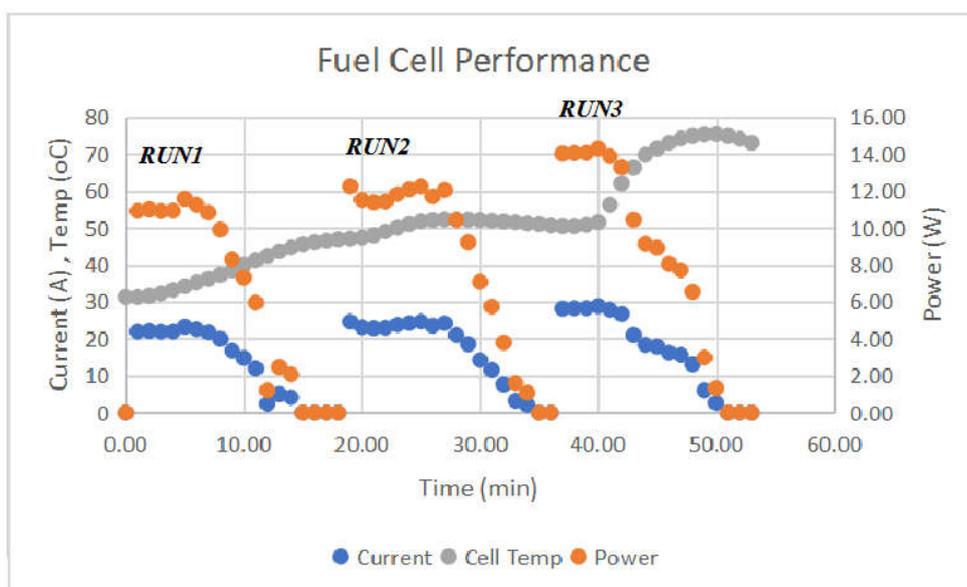


Figure 57 Fuel Cell Performance with NaBH₄ hydrolysis reactor at 0.5V (MEA1)

In the first run (Run1), the maximum current was obtained as 22A with a power of 11W for 7 minutes and then the power and current started to decrease as a result of decrease in H₂ generation rate. The cell temperature at start-up was 31 °C . At the end of Run1 cell temperature was increased to 45 °C . Immediately second run (Run2) was started. The maximum current of 24A was obtained for 8 minutes with a maximum power of 12W in Run2. The cell temperature was increased to 51 °C at the end of Run2. After Run2 finished Run3 was started immediately. The maximum power reached to 14W with a current of 28A for 5 minutes in Run3. During Run3 cell temperature increases rapidly up to 75 °C . Therefore cooling is recommended for further runs.

6.3.2 Results of fuel cell test with new prepared MEA2

By following the methodology that is explained in the Section 6.2, new MEA2 for PEMFC was prepared. The picture of coated catalyst layers was shown in Figure 58.

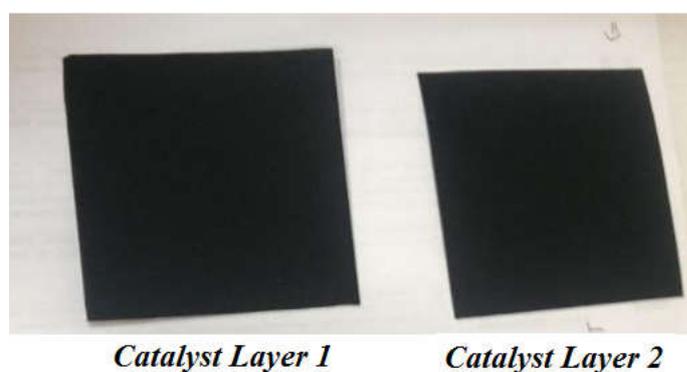


Figure 58 Pictures of coated catalyst layers

Table 20 shows the actual and theoretical weights of prepared catalyst layers as well as the error percentage.

Table 20 Weights of prepared catalyst layers

| | Blank GDL Weight (g) | Theoretical Coated GDL Weight (g) | Actual Weight (g) | Error % |
|------------------|---|--|----------------------------------|--------------------|
| Catalyst Layer 1 | 1.432 | 1.552 | 1.553 | 1.088 |
| Catalyst Layer 2 | 1.531 | 1.651 | 1.653 | 1.506 |

As described in section 6.2, same conditions for Reactor 3 that is 10g NaBH₄ at x=12 when 1.0g of FeCl₃ catalyst was dissolved in water was applied for performance testing of newly prepared MEA's (MEA2).

For performance tests, the fuel cell voltage was kept constant at 0.55V and air flow rate of 0.56 L/min for all experiments.

Before solid NaBH₄ system integrated to the PEM fuel cell, fuel cell was tested with pure hydrogen and compared with the hydrogen supply coming from developed solid NaBH₄ hydrolysis system. Figure 59 shows the fuel cell operation data with pure H₂. Figure 60 shows the fuel cell operation with integrated NaBH₄ hydrolysis system that is composed of fresh catalyst and NaBH₄.

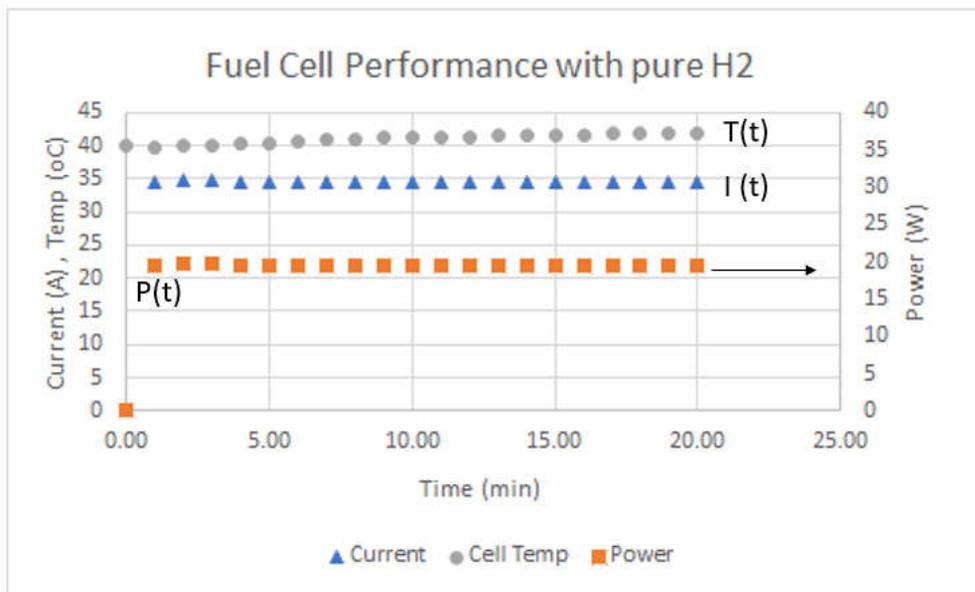


Figure 59 Fuel cell performance for pure H₂ at constant cell voltage of 0.55V with MEA2

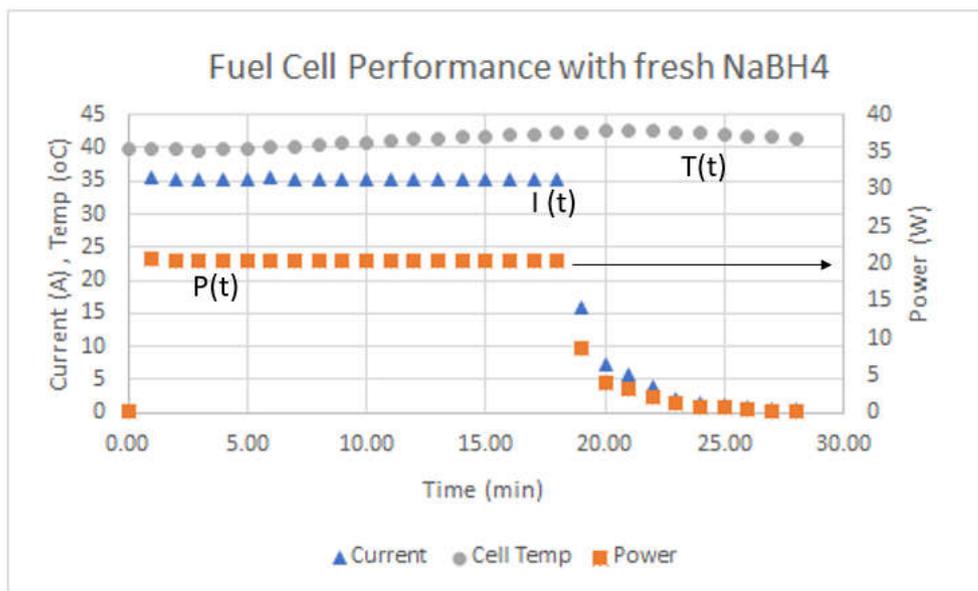


Figure 60 Fuel cell performance of integrated NaBH₄ hydrolysis system at 0.55V with MEA2

It must be noted that fuel cell temperature was around 40 °C for both experiments. By operating the cell with higher voltage than in the previous experiments, the temperature of the system is seen to be controlled better. According to the Equation 6.10, by increasing cell voltage, efficiency increases. Efficiency is also

related with the ratio of electrical work to heat work. Thus, if efficiency increases the amount of work done for heat decreases yielding that the temperature of fuel cell system increases is less than operating at lower cell voltages. Moreover, by the increase in cell voltage, consumption of H_2 decreases as well as power and current decreases. Thus, a longer period of time generation for electricity was obtained for fuel cell at 0.55V cell voltage than operating at 0.5V.

One can compare the fuel cell performance with pure hydrogen and solid $NaBH_4$ system from Figures 59 and 60. The maximum power achieved by pure hydrogen was 20W with a current of 35A. The slightly higher performance was obtained by developed solid $NaBH_4$ hydrolysis system. This is because of generated hydrogen coming from hydrolysis reaction contains some humidity that enhances the fuel cell performance.

After this experiment finished, the solution remaining at the reactor was filtered in order to recover the $FeCl_3$ catalyst. Then, filtered catalyst was placed into the reactor with fresh 10g of solid $NaBH_4$. Again 66.6g water was injected into the reactor in order to see the further performance of filtered catalyst in the fuel cell. Figure 61 shows the performance of first filtered catalyst.

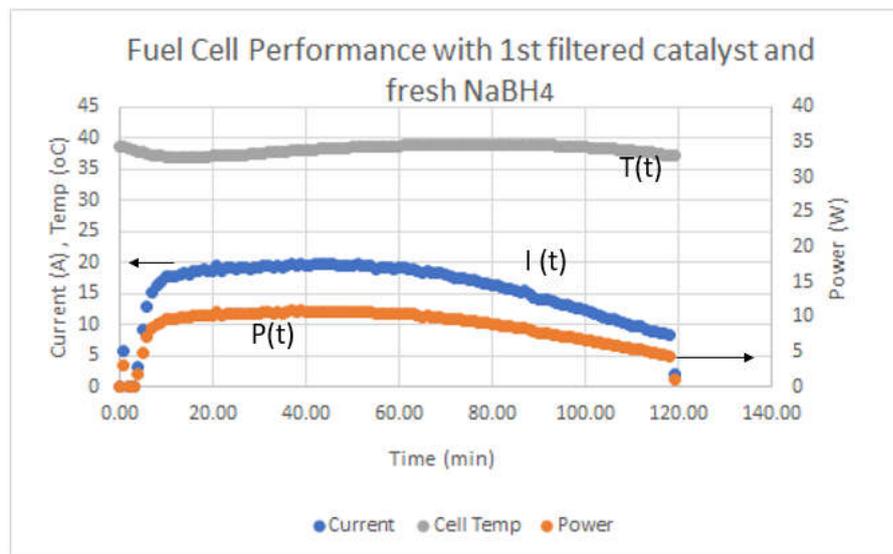


Figure 61 Performance of 1st filtered catalyst in the fuel cell at 0.55V with MEA2

As can be seen from Figure 61 filtered catalyst showed very good performance. It operated at constant current of 20A and 11W for 65 minutes. This supports the theory that black precipitate after the hydrolysis reaction is active catalyst.

For further investigation of the activity of filtered catalyst, the solution remaining in the reactor was filtered for the second time. Figure 62 shows the performance of second filtered catalyst.

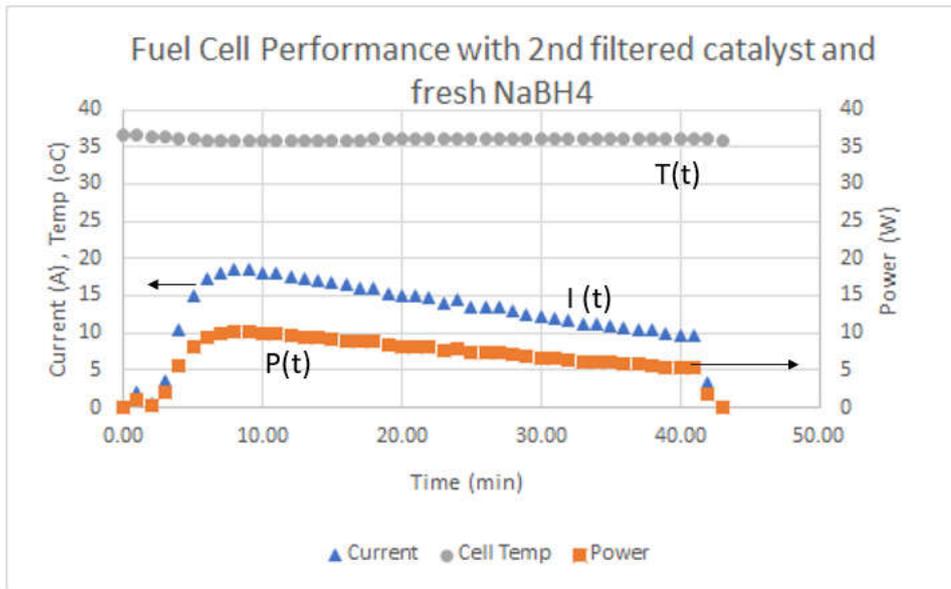


Figure 62 Performance of fuel cell with second filtered catalyst at 0.55V with MEA2

Figure 62 illustrates that, the fuel cell exhibited a decreasing performance with respect to power and current, during the fuel cell test conducted with the second filtrated FeCl_3 catalyst.

The reproducibility of all fuel cell test experiments were shown in Appendix D.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

In this Ph.D thesis, a novel system for hydrogen generation from solid state sodium borohydride was developed and integrated to PEMFC to generate electricity. The developed hydrolysis system addresses three main issues regarding to the hydrolysis of NaBH_4 as follows:

- ✓ The gravimetric hydrogen storage capacity of sodium borohydride is increased by using limited amount of water.
- ✓ System's weight is decreased since there is no need for separate fuel storage tank. The total weight of developed system was 525g.
- ✓ The cost of the system is more accessible when compared to noble-metal catalysts since effective catalysts like FeCl_3 and CoCl_2 is used.

FeCl_3 catalyst was found to be more suitable to be tested in PEMFC.

This fuel cell system is recommended to work between 0.55-0.6 V. If voltage is at 0.5V, the temperature of the fuel cell cannot be controlled. It may increase above 70°C . Temperature of PEMFC remains $35\text{-}40^\circ\text{C}$ if voltage is kept at 0.55V. The power of PEMFC is kept at 20W for more than 30min.

In fuel cell tests, the performance of pure H_2 supply and H_2 supply from developed hydrolysis of NaBH_4 system was compared at 0.55V. It was found that developed solid sodium borohydride system shows slightly higher performance when compared with pure hydrogen supply. This is due to the hydrogen generated from NaBH_4 hydrolysis contains some moisture that humidifies the membrane of fuel cell. Hence, it enhances the fuel cell performance. The developed system that

is uses fresh NaBH_4 and catalyst can supply 20W and 35A for 18 minutes that is enough to charge the battery of a notebook.

Moreover, when FeCl_3 was first contacted with NaBH_4 and water it produces black precipitate. This black precipitate of FeCl_3 was filtered and reused in fuel cell tests with fresh NaBH_4 . This black precipitate that is called “active catalyst” was found to be also promising to investigate further since it generates 11W for 65minutes. This is enough to charge the battery of cell phone.

To conclude, in this doctorate study, solid sodium borohyride hydrolysis system is developed in order to continuously supply hydrogen for PEMFC for portable applications. This system is promising for patent application. It is recommended to further investigate the filtered FeCl_3 catalyst. Also, it is recommend to improve this system for ease of operation.

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APPENDIX A

SAMPLE CALCULATION FOR THE H₂ GENERATION YIELD

Yield is defined as total H₂ generated (L) per grams of NaBH₄ as shown in Equation A.1.

$$Yield = \frac{\text{Total } H_2 \text{ produced}(L)}{\text{Amount of NaBH}_4(g)} \quad (\text{A.1})$$

For example, for R2-14 total H₂ produced was found as 7.34 L when 5g of NaBH₄ was used. So, yield can be calculated as follows:

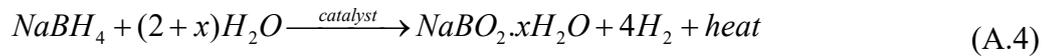
$$Yield = \frac{\text{Total } H_2 \text{ produced}(L)}{\text{Amount of NaBH}_4(g)} = \frac{7.34L}{5.00g} = 1.468L/g \quad (\text{A.2})$$

APPENDIX B

SAMPLE CALCULATION FOR THE EFFICIENCY

$$\text{Efficiency}(\%) = \frac{\text{Total } H_2 \text{ Generated}(L)}{\text{Theoretical } H_2 \text{ Generated}(L)} \times 100 \quad (\text{A.3})$$

Theoretical H_2 generated can be calculated from the stoichiometry of the hydrolysis reaction.



From stoichiometry Equation A.5 was obtained as:

$$N_{H_2} (\text{mol}) = 4 \times N_{NaBH_4} \quad (\text{A.5})$$

$$N_{H_2} (\text{mol}) = 4 \times \frac{\text{Amount of } NaBH_4}{\text{MWt of } NaBH_4} \quad (\text{A.6})$$

In order to calculate the theoretical volume of H_2 generated, H_2 is assumed to be an ideal gas at 1atm and 298K. Ideal gas equation (A.7) was implemented in Equation A.8.

$$PV = NRT \quad (\text{A.7})$$

$$V_{\text{theo}, H_2} (L) = 4 \times N_{NaBH_4} \times \frac{22.4L}{1\text{mol}} \times \frac{298K}{273K} \quad (\text{A.8})$$

For 5g, 10g and 20g NaBH₄, the amount of theoretical H₂ generation can be calculated as follows:

$$V_{theo,H_2}(L) = 4 \times \frac{5g}{37.83g/mol} \times \frac{22.4L}{1mol} \times \frac{298K}{273K} = 12.92L$$

$$V_{theo,H_2}(L) = 4 \times \frac{10g}{37.83g/mol} \times \frac{22.4L}{1mol} \times \frac{298K}{273K} = 25.85L$$

$$V_{theo,H_2}(L) = 4 \times \frac{20g}{37.83g/mol} \times \frac{22.4L}{1mol} \times \frac{298K}{273K} = 51.71L$$

Sample Calculation for the Mean H₂ generation rate,

$$\text{Mean } H_2 \text{ generation rate} = \frac{\text{Total } H_2 \text{ produced} (@t = t_1)}{\text{Duration}(t_1)}$$

For R1-5, the duration is found as 7.1min and total H₂ produced is so mean H₂ generation rate is calculated as:

$$\text{Mean } H_2 \text{ generation rate} = \frac{4.05L}{7.1} = 0.57L / \text{min}$$

APPENDIX C

CALCULATION OF H₂ AMOUNT NECESSARY FOR 100W PEMFC

Faraday's law:

$$n_i = \frac{Q}{F} \times \frac{M_i}{n}$$

Where F=Faraday's constant i.e. 96485C/mol

$$Q = I \times t$$

$$N = \frac{m_i}{M_i \times t}$$

$$N_{H_2} = \frac{I}{nF} = \frac{i \times A}{nF}$$

$$Power = i \times V \times A$$

Assume that fuel cell operating at V=0.6V

$$100W = iA \times 0.6V$$

$$iA = 166.66 \text{ A}$$

$$N_{H_2} = \frac{166.66}{2 \times 96485} = 0.00086 \text{ mol/s} = 0.052 \text{ mol/min}$$

If H₂ is assumed to be ideal gas under 1 atm and 298K,

$$V_{H_2} = 0.052 \text{ mol} / \text{min} \times \frac{22.4 \text{ L}}{1 \text{ mol}} \times \frac{298 \text{ K}}{273 \text{ K}} = 1.27 \text{ L} / \text{min}$$

Similar calculation can be done for operation of 20W and 10W fuel cell system.

For 20W fuel cell operating at 0.55V:

$$20 \text{ W} = iA \times 0.55 \text{ V}$$

$$iA = 36.36$$

$$N_{H_2} = \frac{36.36}{2 \times 96485} = 1.88 \times 10^{-4} \text{ mol} / \text{s} = 0.011 \text{ mol} / \text{min}$$

If H_2 is assumed to be ideal gas under 1 atm and 298K,

$$V_{H_2} = 0.011 \text{ mol} / \text{min} \times \frac{22.4 \text{ L}}{1 \text{ mol}} \times \frac{298 \text{ K}}{273 \text{ K}} = 0.28 \text{ L} / \text{min}$$

For 10W fuel cell operating at 0.55V:

If H_2 is assumed to be ideal gas under 1 atm and 298K,

$$V_{H_2} = 0.0055 \text{ mol} / \text{min} \times \frac{22.4 \text{ L}}{1 \text{ mol}} \times \frac{298 \text{ K}}{273 \text{ K}} = 0.14 \text{ L} / \text{min}$$

APPENDIX D

REPRODUCIBILITY OF EXPERIMENTS

Each experiment reported in Chapter 5, were repeated 3 times. Figure A4.1 shows the reproducibility of one of the experiment. For these test, 5g NaBH₄ and 0.5g solid FeCl₃ was placed in the Reactor 3. 33.3g (x=12) of bottled water was injected into the reactor. This reaction was repeated 3 times.

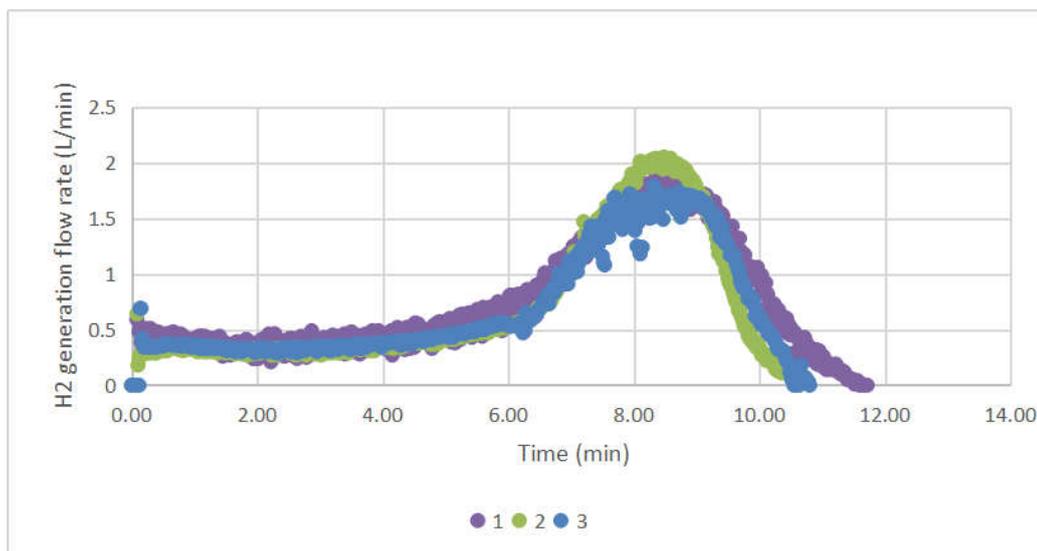


Figure A4.1 Reproducibility of experiments (5g NaBH₄, 33.3g H₂O, x=12, 0.5g solid FeCl₃)

As can be seen in Figure A4.1, the experiments are reproducible.

REPRODUCIBILITY OF PEMFC EXPERIMENTS

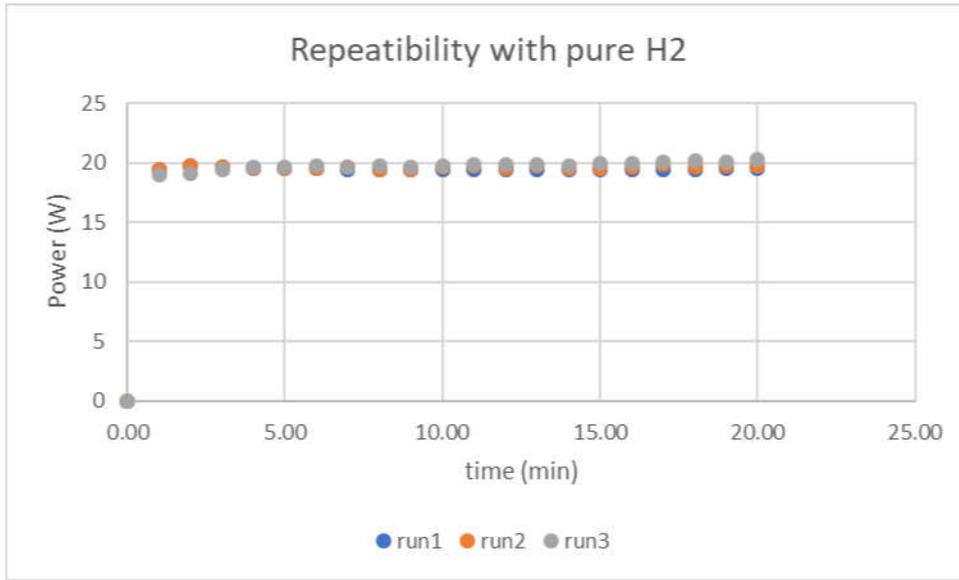


Figure A4.2 Reproducibility of fuel cell test with pure hydrogen at 0.55V with MEA2

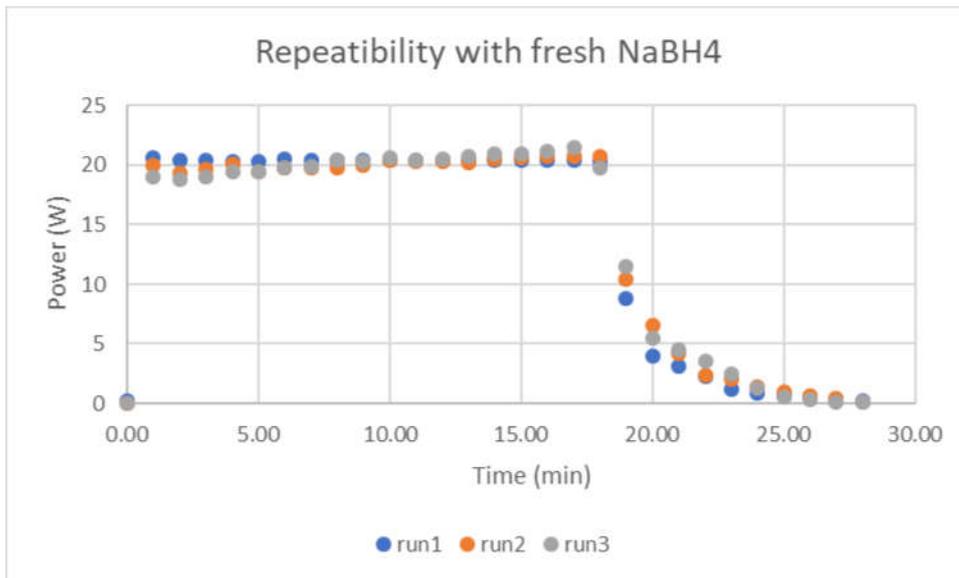


Figure A4.3 Reproducibility of fuel cell test with fresh NaBH₄ at 0.55V with MEA2

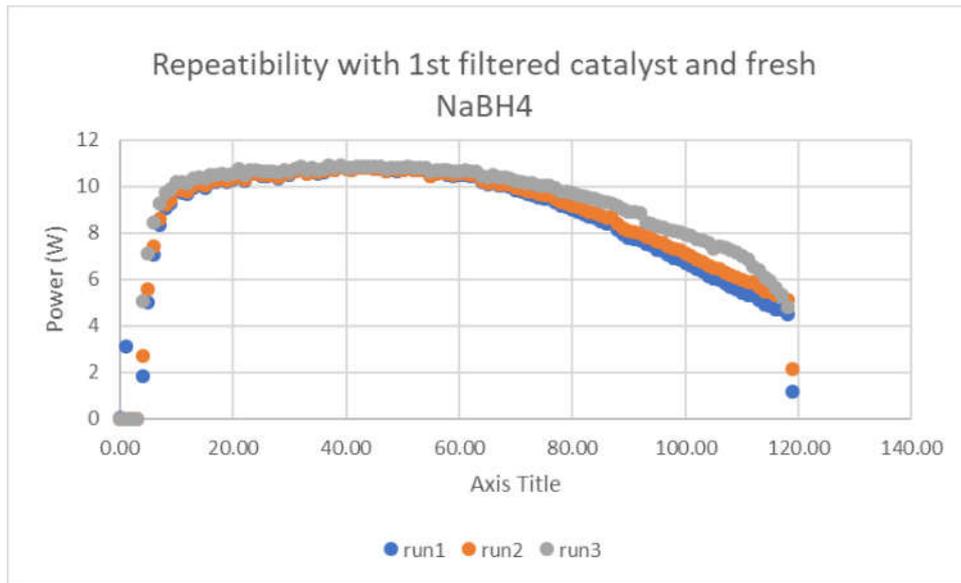


Figure A4.4 Reproducibility of fuel cell test results with first filtration of FeCl_3 catalyst and fresh NaBH_4 at 0.55V with MEA2

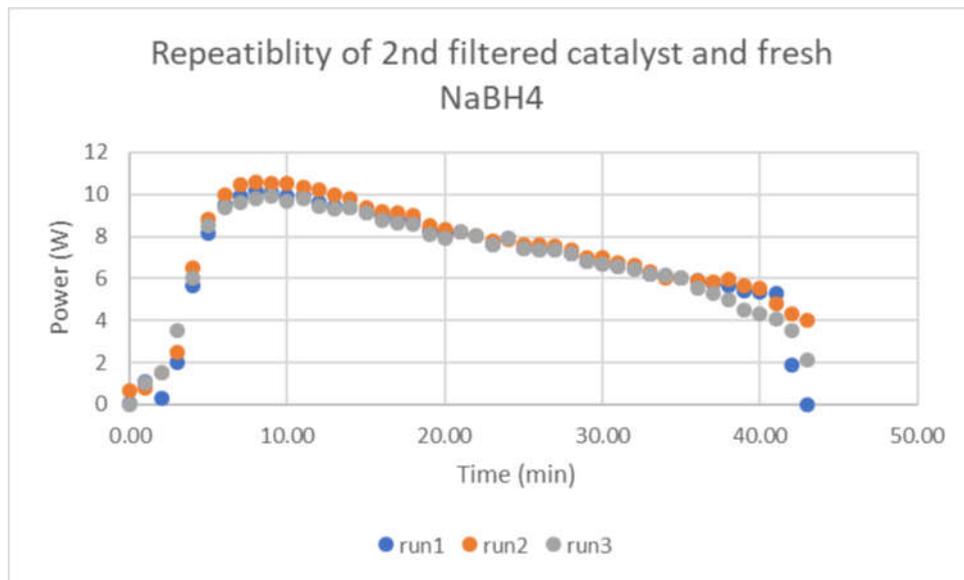


Figure A4.5 Reproducibility of fuel cell test results with second filtration of FeCl_3 catalyst and fresh NaBH_4 at 0.55V with MEA2

APPENDIX E

SPECIFICATIONS OF WATER

Table A.1 Specifications of water

| Water type | pH | Conductivity |
|------------------------------------|-----------|------------------------------|
| Bottled drinking water | 7.39 | 37.1 $\mu\text{s}/\text{cm}$ |
| Ultra-pure de-ionized water | 5.02 | 5.2 $\mu\text{s}/\text{cm}$ |
| Tab water | 7.48 | 875 $\mu\text{s}/\text{cm}$ |

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- Summer Internship at BATICIM – West Anatolia Cement Manufacturing Company, Izmir/Turkey.

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Boran A., Erkan S., Ozkar S., Eroglu I., “Kinetics of hydrogen generation from hydrolysis of sodium borohydride on Pt/C catalyst in a flow reactor” International Journal of Energy Research 37:443-448, 2013.

Boran A, Erkan S, Ozkar S, Eroglu I, Kinetics of hydrogen production from hydrolysis of sodium borohydride over intrazeolite Co(0) nanoclusters in a flow reactor.. *"International Conference on Hydrogen Production Technologies (ICH2P-11)"*, (2011), p.242STO.

Presentations:

Oral Presentation: Yurdakul A., Erkan S., Ozkar S. Eroğlu I. “On demand continuous hydrogen production system using hydrolysis of sodium borohydride for portable PEM Fuel Cell applications”, 10th International Conference on Clean Energy – ICCE 2010, 14-17th September, 2010, Gazimagusa, Northern Cyprus.

Oral Presentation: Yurdakul A., Erkan S., Ozkar S. Eroğlu I, “Design of a Hydrogen gas generator using aqueous sodium borohydride solution for portable fuel cell applications”, Proceedings of 4th National Hydrogen Energy Conference (additional abstract book), 15-16 October, Kocaeli, 2009.

Poster: Yurdakul A., Erkan S., Ozkar S. Eroğlu I,” Design of a Hydrogen gas generator using aqueous sodium borohydride solution for portable fuel cell applications”, 18th World Hydrogen Energy Conference, Essen, Germany, 16-21 May 2010.

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3rd ranked student in the Fall of 2008.

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