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DEPARTMENT OF ENGINEERING SCIENCE AND MECHANICS

HYDROGEN GENERATION WITH
NANOTEXTURED COBALT CATALYST

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Abstract

Developing environmentally friendly, sustainable, and inexpensive energy sources is one of the greatest challenges today. Thus far, the most promising approach seems to be the use of hydrogen to generate electricity via a proton exchange membrane (PEM) fuel cell. While fuel cell technology is fast approaching commercial viability, there are still issues with developing cost-effective ways to safely store and extract hydrogen, especially for transportation applications. The chemical hydride storage method offers various materials with high energy densities that could potentially be dispensed via liquid form using an infrastructure akin to today’s gasoline refueling stations. Hydrogen can then be rapidly extracted from these storage systems by means of a metal catalyst. Unfortunately, despite the many advantages of this system, the high cost of the noble-metal catalysts usually used have made it not economically viable.

Nonetheless, it is well known that the rate hydrogen is generated via a metal catalyst is directly proportional to the active surface area of the catalyst. It has also been demonstrated in literature that the amount of active surface area of the catalyst can be increased through deposition of the catalyst onto a nanotextured surface. The increased amount of active surface area available to react to the hydride solution may be used to overcome the lower catalytic activity of less expensive, non-noble metals such as cobalt. In this thesis, work is done to design a nanotextured cobalt catalyst that is inexpensive but can generate hydrogen from a chemical hydride solution at rates comparable to other hydrogen generation systems.
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1 Introduction

Developing environmentally friendly, sustainable, and inexpensive energy sources is one of the greatest challenges today. Even now, with the price of hydrocarbon fuels climbing higher and higher each year, alternative energy technologies are still too expensive to compete with fossil-fuel technologies. The most promising approach thus far seems to be the use of hydrogen to generate electricity via a proton exchange membrane (PEM) fuel cell [1]. Hydrogen is an attractive alternative fuel because it is lightweight, highly abundant, clean and efficient [2, 3].

1.1 How Does a PEM Hydrogen Fuel Cell Work?

PEM fuel cells are fuelled by hydrogen and oxygen (or air) and produce only water and heat as byproducts [1, 4]. Figure 1 illustrates the basics behind how a PEM fuel cell works. Hydrogen gas flows through channels to the anode, where a catalyst causes the hydrogen molecules to separate into protons and electrons. While the protons are conducted through the membrane – which allows only the protons to pass through – to the other side of the cell, the negatively-charged stream of electrons follows an external circuit to the cathode. It is through this external circuit that work is done. On the other side of the cell, oxygen gas (or air) flows through channels to the cathode. When the electrons return from doing work through the external circuit, they react with the oxygen and the hydrogen protons at the cathode to form water. This is an exothermic reaction that also generates heat that can be used outside the fuel cell [4, 5]. The following equations describe the reactions that specifically occur at the anode and cathode:

\[
\text{Anode: } H_2 \rightarrow 2H^+ + 2e^- \quad (1)
\]

\[
\text{Cathode: } O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)
\]
Theoretically, the maximum voltage these reactions can generate is 1.2 V. But in practice, the PEM fuel cell usually generates 0.7 V to 0.9 V and about 1 W/cm² of power [5].

*Figure 1: How a PEM Fuel Cell Works*

Unfortunately, while hydrogen fuel cell technology is fast approaching commercial viability, there is still the issue of developing a cost-effective way to safely store and extract hydrogen for the fuel cell to use. Chemical hydrogen storage is the method of hydrogen storage that is utilized in this thesis.

### 1.2 Chemical Hydrogen Storage – Using Sodium Borohydride

In 2002, the Department of Energy (DOE) established various targets for onboard hydrogen storage systems used in light-duty vehicles necessary to be competitive with fossil fuel technologies. These targets, which were later modified in 2009, were for the entire
hydrogen storage system, not just the material used to store the hydrogen (See Table 1) [6, 7].

<table>
<thead>
<tr>
<th>Storage Parameters</th>
<th>Units</th>
<th>2010</th>
<th>2015</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>System gravimetric capacity</td>
<td>kWh/kg</td>
<td>1.5</td>
<td>1.8</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>wt% H₂</td>
<td>4.5</td>
<td>5.5</td>
<td>7.5</td>
</tr>
<tr>
<td>System volumetric capacity</td>
<td>kWh/L</td>
<td>0.9</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>g H₂/L</td>
<td>28</td>
<td>40</td>
<td>70</td>
</tr>
<tr>
<td>H₂ delivery temp.</td>
<td>°C</td>
<td>-40/86</td>
<td>-40/85</td>
<td>-40/95-105</td>
</tr>
<tr>
<td>Operating Pressure</td>
<td>MPa</td>
<td>0.5/1.2</td>
<td>0.5/1.2</td>
<td>0.3/1.2</td>
</tr>
<tr>
<td>Kinetics</td>
<td>(g H₂/s)/kW</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Cost</td>
<td>$/kWh net</td>
<td>To be determined</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Note that 1kg of H₂=1 gallon of gasoline=33.3 kWh*

Chemical hydrides store hydrogen via strong chemical bonds. Hydrogen gas is released from these hydrides through a chemical reaction with water or alcohols. Typically the byproducts of these reactions cannot be directly recharged with hydrogen gas on-board a vehicle. The hydride must be regenerated to its hydrogenated form off-board [3, 8]. On a more positive note, this method of storage would be easier to transition to from fossil fuels as chemical hydride solutions could potentially be dispensed via liquid form using an infrastructure akin to today’s gasoline refueling stations [3].

One of the most commonly studied chemical hydride reactions is the reaction of sodium borohydride (NaBH₄) and water. This reaction, shown in Equation 3, can be controlled via pH and through the use of a catalyst. NaBH₄ solution is highly stable at a pH greater than 9 and can be easily and safely transported without any hydrogen release. Hydrogen can then be extracted from such a solution using a metal catalyst [1, 3, 6, 9, 10, 11]. An advantage of using a catalyst based hydrogen generation system for practical applications is that the catalyst can
be used as a switch. Hydrogen will only be released when the catalyst is in contact with the solution.

\[
NaBH_4 + 2H_2O \xrightarrow{\text{catalyst}} NaBO_2(s) + 4H_2(g) \quad \Delta H = -217 \text{ kJ/mol}
\] (3)

The standard-state enthalpy change of \(\Delta H = -217 \text{ kJ/mol}\) at 25 °C is calculated from standard enthalpies -188.61 kJ (NaBH₄), -571.66 kJ/mol (2H₂O), -977.0 kJ (NaBO₂) and 0 kJ (4H₂) [11]. Based on this hydrolysis reaction, NaBH₄, which has 10.9 wt% hydrogen, will in theory produce 8 hydrogen atoms. This reaction also operates through zero order kinetics and no input of heat is required to extract hydrogen at room temperature. In addition, the hydrogen generated is very pure since there are no side reactions [6, 11, 12].

Sodium metaborate is another environmentally benign byproduct of this reaction. While it can be recycled back to sodium borohydride, possibly through a reaction with MgH₂, multi-step conditions are required. These conditions prevent on-board regeneration from being possible [3, 6].

What’s preventing this system from being commercially viable is that it is too expensive to contend with hydrocarbon fuels. The current price of NaBH₄ is about $55 per kg, which combined with its poor recyclability prevents it from competing with fossil fuels. Even if technology was developed to reduce production costs of NaBH₄ to 1/10th of its current price – for which claims have been made – it would still cost about $25.80 per kg of H₂ produced. Therefore, given that 1 kg of H₂ is equivalent to 1 gallon of gasoline, using a NaBH₄ system will cost about 6.45 times the current price of gasoline (~$4 per gallon). (See Appendix for calculations.) The high costs of the metal catalysts typically used in the reaction, such as Ruthenium and Platinum, make up a large portion of the H₂ storage system’s costs. Therefore, the economic viability of a chemical hydrogen storage system depends on the development of
cheaper alternatives for noble-metal catalysts that won’t compromise hydrogen discharge kinetics [1, 6].

In addition, once a cheaper catalyst structure is developed, NaBH₄ can be replaced with a more practical and cheaper chemical hydride. In 2007, a “No-Go” recommendation was made to the U.S. Department of Energy Hydrogen Program by an independent review panel on the use of NaBH₄ as a storage technology. Of special concern to the panel was the high energy penalty and cost of regenerating sodium borate (NaBO₂) back to NaBH₄ fuel [13]. Despite this recommendation, NaBH₄ is still used in this study because it is a well-studied reaction that offers the perfect model system for experimental work. NaBH₄ can later be replaced with a different chemical hydride once a practical inexpensive catalyst system is developed.

1.3 How Does the Catalytic Mechanism Work?

There are two different types of catalysts, homogeneous and heterogeneous. In the case of a homogeneous catalyst, both the catalyst and the reactants are in the same phase which is typically some sort of liquid or aqueous solution. With heterogeneous catalysts, the catalyst and reactants are in different phases; the catalyst is typically in the solid phase while the reactants are in the liquid or gas phase [14]. Heterogeneous cobalt catalyst structures are used in this thesis.

![Catalytic Mechanism Diagram](image)

Figure 2: Catalytic Mechanism
Figure 2 illustrates the catalytic mechanism behind the reaction in Equation 3. First, the H$_2$O and BH$_4^-$ (NaBH$_4$ dissociates into Na$^+$ and BH$_4^-$ ions) reactants diffuse to and adsorb onto active sites on the surface of the catalyst. Electrons are discharged from the BH$_4^-$ ion and through the catalyst, resulting in the H$^-$ in BH$_4^-$ being oxidized. Meanwhile, these electrons reduce the H$^+$ in water and generate hydrogen gas (Equation 4) [11].

$$H^+ + H^- \Rightarrow H_2 \quad (4)$$

In the end, the products BO$_2^-$ and H$_2$ desorb from the surface of the heterogeneous catalyst and move away, freeing up space for further reactions. BO$_2^-$ reacts with the remaining Na$^+$ ions in the solution to form NaBO$_2$ [14]. Surface area is critical for heterogeneous catalysts since it determines the availability of the catalytic sites where these reactions take place. Figure 3 illustrates how the activation energy of the reaction is lowered by the alternative reaction path offered by the catalyst. The catalyst itself remains unchanged at the end of this reaction.

\[\text{Figure 3: Energy Diagram for heterogeneous catalyst}\]
1.4 Increasing Active Catalytic Surface Area for Inexpensive Catalysts

As stated earlier, the more catalytic surface area is available, the faster a reaction will occur. Therefore, it can be inferred that the rate of hydrogen generated from the NaBH$_4$ solution will be directly proportional to the amount of active surface area of the catalyst in contact with the solution. It is also well known that a nanotextured surface has more surface area available than a planar one. Therefore, by metallizing a nanotextured surface with a metal catalyst, more active catalytic surface area will be free to react with the hydride solution.

Cobalt is inexpensive compared to the noble metals typically used as catalysts for generating hydrogen. However, it also has less catalytic activity. But by depositing cobalt on a nanotextured surface, this lower catalytic activity can be offset by the increased amount of active surface area available to react to the hydride solution. Creating such an inexpensive catalyst structure that is comparable to other more expensive systems is the main goal of this thesis.
2 Cobalt on Nanotextured Polymer Films

An electroless route for preparing a cobalt metal-based catalyst supported on nanotextured poly(chloro-p-xylylene), denoted as Co-nanoPPX from hereon, was recently proposed in literature [9, 10]. The hydrogen release rate of this catalyst structure has been reported to vary from 4,250 mL(g•min)\(^{-1}\) to as high as 7,450 mL(g•min)\(^{-1}\) [6, 9]. These rates are comparable to the release rate of other prominent metal-based catalysts published in literature, as listed in Table 2. It should also be noted that the hydrogen release rate of the Co-nanoPPX catalyst is significantly higher than the 32 mL(g•min)\(^{-1}\) release rate of metallic cobalt catalyst [6, 10].

As presented in the table, platinum (Pt/C with rate of 23,090 mL(g•min)\(^{-1}\)) and ruthenium (IRA-400 with rate of ~9,600 mL(g•min)\(^{-1}\)) based catalysts have higher hydrogen release rates than the Co-nanoPPX catalyst. However, given the ease of fabrication of the Co-nanoPPX, which is described in the next section, this catalyst structure is still promising enough to justify future studies.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[NaBH(_4)] (wt%)</th>
<th>[NaOH] (wt%)</th>
<th>Temperature (°C)</th>
<th>( \text{H}_2 ) (g) release rate (mL/g•min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-26*</td>
<td>20</td>
<td>10</td>
<td>25</td>
<td>4032</td>
<td>[15]</td>
</tr>
<tr>
<td>IRA-400*</td>
<td>12.5</td>
<td>1</td>
<td>25</td>
<td>~9600</td>
<td>[12]</td>
</tr>
<tr>
<td>Pt/C</td>
<td>10</td>
<td>5</td>
<td>Data unknown</td>
<td>23,090</td>
<td>[16]</td>
</tr>
<tr>
<td>CoB**</td>
<td>2</td>
<td>5</td>
<td>15</td>
<td>~3500</td>
<td>[17]</td>
</tr>
<tr>
<td>Co-nanoPPX</td>
<td>2.5</td>
<td>10</td>
<td>25</td>
<td>~7450</td>
<td>[6]</td>
</tr>
</tbody>
</table>

*Ru-based catalyst system  **Unsupported catalyst

Table 2: Comparing the hydrogen gas release rate from NaBH\(_4\) of various catalysts
2.1 Experimental Procedures

2.1.1 Creating the Cobalt on Nanotextured Polymer Catalyst

The fabrication of Co-nanoPPX involves a layering process. First an allyltrimethoxysilane self-assembly monolayer is deposited onto a silicon substrate. NanoPPX makes up the second layer and then cobalt nanoparticles are deposited on top of the polymer as the final layer. The following sections describe in detail the steps involved for creating each layer of the catalyst structure.

2.1.1.1 Self-Assembly Monolayer (SAM)

The first step of creating the Co-nanoPPX is to create a bond between the nanoPPX film and the silicon substrate. Because the nanoPPX film is naturally hydrophobic, the substrate’s surface needs to be first modified with an allyltrimethoxysilane (H₂C=CH-CH₂-Si(OCH₃)₃), see Figure 4, self-assembled monolayer (SAM). The adhesion of the nanoPPX film to the silicon substrate is the result of the allyl group (H₂C=CH-CH₂-) chemically binding with the film. Without the SAM layer, the hydrophobic nature and the lack of any covalent bonding of nanoPPX to the substrate will make it easy for the film to delaminate in solvents [6, 10]. Figure 5 illustrates the delamination that occurs when the polymer film is deposited on an unmodified substrate. Notice how along the edges the polymer is starting to pull away from the substrate after it was submerged in a solution.

---

1 A self-assembled monolayer is defined as an organized layer of amphilic molecules where the “head group” has a specific reversible affinity for a substrate.
Figure 5: Illustration of the delamination when nanoPPX is deposited on an unmodified silicon substrate.

SAM is deposited onto the silicon substrate through a series of solutions. First the samples are rinsed several times in deionized water and ethanol. Then the samples are put into a mixture of piranha solution at 80°C for 30 minutes. The piranha solution consists of a 3:1 ratio (v/v) of H$_2$SO$_4$ and H$_2$O$_2$. The samples are then washed with deionized water and dried under air. Next the cleaned samples are placed in the SAM solution at 25°C. The SAM solution is prepared by adding 1% (v/v) allyltrimethoxysilane in toluene containing 0.1% (v/v) acetic acid. After the samples have incubated in the SAM solution for 3 hours, they are removed and sonicated in toluene for 5 minutes. The samples are then dried on a hot plate at 140°C for 5 minutes [6].

2.1.1.2 NanoPPX Deposition

A modified Labcoter$^\text{TM}$-II deposition unit is used to deposit the nanoPPX films onto the SAM modified silicon substrates. The deposition unit is basically made up of three sections: a vaporizer, a pyrolysis furnace, and a deposition chamber. The deposition chamber was modified to include oblique angle polymerization (OAP) during the polymer film growth. OAP induces a directional constraint – incidence angle, $\alpha<<90^\circ$ - to the diradical flux. This results in the formation of a low-density and porous PPX film made of nanorods tilted away from the substrate normal instead of the growth of a planar film. OAP Modifications included the
installation of a nozzle with a 45° bend at the tube furnace’s outlet and the addition of a substrate holder connected to a stepper motor that allows axial rotation (ω) and angular motion (α) to vary the incidence flux’s direction [6]. Figure 6 shows a schematic of a Labcoter™-II deposition unit modified for OAP.

![Figure 6: Labcoter™-II system with deposition chamber modified for oblique angle polymerization. Used to deposit nanoPPX films onto SAM modified silicon substrates.](image)

The following steps are used to deposit the nanoPPX film onto a SAM modified silicon substrate. Steps 3 to 6 of this process are automated by the deposition unit. 0.3 grams of precursor is used to deposit the nanoPPX and 10° is used for the values of α and ω [6].

1. Load the PPX precursor into the vaporizer and affix the substrate sample to the substrate holder. Use the stepper-motor controller to adjust the α and ω values.
2. Evacuate the vaporizer, pyrolysis furnace, and deposition chamber to a pressure less than 25 mtorr.

3. Preheat the pyrolysis furnace to 690 °C and pre-cool the cold trap to less than -90 °C.

4. Slowly heat the vaporizer to 175 °C. The shaft motor for planar deposition is also powered by the vaporizer power switch.

5. After the vaporizer reaches 175 °C, allow the PPX film to deposit on the substrate for 10 minutes.

6. Turn off the power to the vaporizer and pyrolysis furnace.

7. Once the pyrolysis furnace is cooled to less than 300 °C, bring the complete system to atmospheric pressure by using a vacuum relief valve.

When the precursor PPX vapors first touch the silicon substrate, a thin layer of PPX (~1-5 nm RMS roughness) forms because of the high surface diffusion of monomeric diradicals and/or PPX-oligomers on the substrate. This thin layer has surface instabilities that act as nucleation sites that PPX nanorods subsequently grow from. Various morphologies of nanoPPX can be formed by changing the deposition parameters. Examples of such morphologies can be found in Reference [6]. The columnar morphology shown in Figure 7 is the morphology used in this project.

![Figure 7: Columnar Morphology for nanoPPX](image)
2.1.1.3 Electroless Deposition of Cobalt Nanoparticles

The last step in creating the Co-nanoPPX catalyst involves metallizing the nanoPPX with cobalt nanoparticles. This metallization is done through a series of steps (See Figure 8). First the samples are functionalized with an aromatic ligand (pyridine) by being bathed in a 10% (v/v) pyridine bath for 48 hours. The samples are then briefly rinsed in water before being transferred to a palladium bath for 45 minutes. The palladium bath is prepared by adding 5mL NaCl (1M) to 45 mL of palladium solution. The palladium solution must be made at least a day beforehand as it needs to be left in a 25°C water bath for 24 hours before it can be used. The solution is prepared by dissolving 11.8 mg Na tetra chloro-palladate in 1 mL NaCl (1M), adding 10 mL of 2-(N-morpholino)ethanesulfonic acid (MES) buffer (0.1 M, pH:5) and then diluting the solution until the total volume of the solution is 100mL. The palladium within the solution catalyzes the surface of the samples by covalently bonding to the pyridine ligands.

After the palladium bath treatment, the samples are then transferred to an electroless cobalt plating bath. The cobalt solution was prepared by dissolving 0.9 g tetrasodium salt of ethylenediaminetetraacetic acid (EDTA), 1 g AlCl₃, and 0.6 g CoCl₂ in 15 mL of water. A separate solution of 0.4 g dimethylamine-borane (DMAB) dissolved in 5 mL of water is then added. The pH of the resulting 20 mL solution is then brought to 8.2 with NaOH using drop-wise addition. The finished cobalt bath should be dark pink in color [6, 9, 10].
The amount of cobalt deposited on the nanoPPX can be controlled by varying the bath time. This rate of deposition exponential decays over time and the amount of cobalt deposited saturates at 90% after a 40 minute bath time [10]. After a specified bath time, the samples are removed from the cobalt solution, rinsed in deionized water and dried under N₂ gas.

2.1.2 Measuring the Amount of Hydrogen Gas Generated

Sodium borohydride solution is prepared by first dissolving 1 g of NaOH in 100 mL of deionized water. After checking that the pH of the NaOH solution is over 12 (otherwise H₂ will spontaneously release from the solution), 2.5 g of NaBH₄ is dissolved into the solution. The setup shown in Figure 9 is then used to measure the amount of hydrogen generated after adding the fabricated catalyst samples to the NaBH₄ solution, which is contained in an Erlenmeyer flask. H₂ gas is collected through gas displacement of water in a volumetric glass tube filled with water, which is suspended upside down in a water filled beaker. The amount of water displaced is measured every minute and the experiment itself is run for 1 hour at a time or until water is displaced past the measuring ability of the volumetric gas tube.

Figure 9: Experimental setup used to measure the amount of H₂ gas generated
2.2 Results and Analysis

In this project, a columnar morphology was used for the nanoPPX and the samples were left in the cobalt bath for 60 minutes. Figure 10 shows one of the Co-nanoPPX catalyst samples created. The silicon substrate upon which the catalyst was deposited had a total area of 4.6875 cm$^2$. About 0.0026 grams of cobalt were deposited over this area. The amount of cobalt deposited on the nanoPPX was determined by measuring the samples before and after the electroless deposition step of the fabrication process.

![Figure 10: Sample Co-nanoPPX catalyst](image)

Figure 11, shows a plot of the volume of hydrogen generated versus time. Through linear regression, a slope of 1.0379 mL(min)$^{-1}$ is calculated. Given the previously stated total area of the sample and total weight of cobalt deposited, hydrogen generation rates of 0.2214 mL(min•cm$^2$)$^{-1}$ and 392.7189 mL(min•g(Co))$^{-1}$ are respectively calculated. (See Appendix for calculation.)

The hydrogen generation rate of 0.2214 mL(min•cm$^2$)$^{-1}$ calculated here is comparable and actually slightly higher to the values found in literature using the same catalyst structure. In Reference [6], the rate of hydrogen generated after a 60 minute cobalt bath ranged from ~0.15-0.175 mL(min•cm$^2$)$^{-1}$. 

15
Figure 11: H$_2$ generated using Co-nanoPPX (60 minute) sample

Hydrogen Generation Rate: 0.2214 mL/(min•cm$^2$)

392.7189 mL/(min•g (Co))

$y = 1.0379x + 2.6266$

$R^2 = 0.9944$
3 Cobalt Deposited on Polycarbonate Membrane

The concept of using a three dimensional catalyst structure to increase the amount of surface area in contact with the NaBH₄ solution led to the idea of using polycarbonate membrane filters. Polycarbonates are a group of thermoplastic polymers. Polycarbonate membrane filters are particularly useful as they contain uniform, cylindrical, “straight through,” pores that contribute to uniform sample deposition over an entire membrane filter surface. These membrane filters are also biologically inert and offer excellent thermal stability and chemical resistance [18]. These characteristics make these membranes promising as a possible catalyst support structure.

3.1 Experimental Procedures

3.1.1 Creating the Cobalt on Polycarbonate Membrane Catalyst

The process for fabricating the cobalt on polycarbonate membrane catalyst is the same as the process used to create the Co-nanoPPX catalyst starting from the electroless deposition step. (See 2.1.1.3 Electroless Deposition of Cobalt Nanoparticles.) The only difference is that the nanoPPX on silicon substrate is replaced with a GE polycarbonate membrane (catalog #K04CP02500) with 0.4 micron pores and 25 mm diameter. The polycarbonate membranes are also taped to glass slides before putting them into the solutions to prevent the membranes from rolling up when wet. As a result, it is assumed that only one side of the membrane, along with hopefully the sides of the membrane pores, is covered with cobalt nanoparticles. The cobalt deposition times (1 minute, 2.5 minute, and 10 minute) used for these samples are shorter than those used for Co-nanoPPX (60 minute) to prevent the pores of the membrane from becoming clogged with cobalt nanoparticles (this would counteract the “3D effect” of
using the polycarbonate membranes). It would be interesting to examine a sample under SEM in the future to see how well the cobalt nanoparticles coated the inside of the pores.

### 3.1.2 Measuring the Amount of Hydrogen Gas Generated

The process for measuring the amount of hydrogen gas generated by the cobalt on polycarbonate catalyst structure is the same as the one used for the Co-nanoPPX. (See 2.1.2 Measuring the Amount of Hydrogen Gas Generated)

### 3.2 Results and Analysis

Figure 13, Figure 14, and Figure 15 show the plots of hydrogen generated versus time for samples of cobalt deposited on polycarbonate membrane where the cobalt bath times were respectively 1 minute, 2.5 minute, and 10 minute. For each hydrogen generation experiment, two polycarbonate membrane samples were deposited at a time into the NaBH₄ solution. Thus, given the 2.5 cm diameter of each sample, the total area of catalyst was 9.82 cm². Therefore, the hydrogen generation rates for the 1 minute, 2.5 minute, and 10 minute samples were respectively 0.0619 mL(min•cm²⁻¹), 0.0722 mL(min•cm²⁻¹), and 0.1835 mL(min•cm²⁻¹). Note that the last rate (10 minute cobalt bath time) is comparable to the rates found in section 2 with the Co-nanoPPX catalyst structure (60 minute cobalt bath time).

Also note the “delayed” reaction in Figure 14. At first, the catalyst samples were floating at the top of the solution and the H₂ bubbles initially generated seemed “stuck” underneath the catalysts to their bottom surfaces. Thus the gas was not moving to displace water from the volumetric glass tube and was also preventing more NaBH₄ solution from coming into contact with the catalysts to generate more H₂. Hence the initial zero slope (H₂ generation rate) during the first 7-8 minutes of H₂ collection. When the situation was observed, the Erlenmeyer flask containing the NaBH₄ solution along with the catalyst was
gently shaken to dislodge the H₂ gas bubbles. As can be seen from the linear nature of the rest of the figure, the catalyst generated hydrogen gas normally from then on.

Figure 13: H₂ generated using cobalt on polycarbonate membrane (1 minute) sample

Figure 14: H₂ generated using cobalt on polycarbonate membrane (2.5 minute) sample
The hydrogen generation rates found for these samples were lower than expected. One theory for why this happened is that surface tension and the micron size nature of the pores prevented the cobalt deposition solutions from reaching the inside of the pores. Figure 16 illustrates this concept.

Theoretically, in order for liquid to enter the pore, hydrostatic pressure must exceed an allowed excess pressure of $2T/R$ on the concave side of the water surface at the pore's opening. $T$ is equal to the surface tension of the liquid and $R$ is equal to the radius of the “hole” being entered [19]. Since $R$ is on the micron scale, a large hydrostatic pressure is needed for the liquid to enter the pore. Therefore, it is very likely that cobalt was not deposited inside the pores and the sought after “3D nature” of the catalyst structure was lost, thereby lowering hydrogen generation rates. Similarly, surface tension may have prevented NaBH$_4$ solution from entering the pores and coming into contact with any cobalt that did deposit along the sides of the pores.
4 Cobalt Deposited on Syringe Filters

The idea of using syringe filters as the base of a cobalt catalyst structure came from the work of Koray Sekeroglu, a PhD student in Professor Melik Demirel’s Biointerface Engineering Lab. He created a micropump from polydimethylsiloxane (PDMS) and attached a syringe filter along with some plastic tubing. With this structure, he was able to constantly recirculate a solution through the filter. This idea was further expanded in this experiment to create a cobalt catalyst structure.

![Figure 17: Syringe Filter attached to a PDMS micropump](image)

4.1 Experimental Procedures

4.1.1 Depositing the Cobalt Catalyst on the Syringe Filter

The same solutions used in the electroless deposition of cobalt during the fabrication process of Co-nanoPPX are used here (See 2.1.1.3 Electroless Deposition of Cobalt Nanoparticles). However, given the structure of the syringe filters, a different method was needed for soaking the insides of the syringe filters with the solutions. The experimental setup shown in Figure 18 illustrates how syringes, plastic tubing, and clamps were used to hold the solution within the filters so that they could soak for the appropriate times. The syringes were used to push solution through the filters and into the attached plastic tubing. The plastic
tubing was then clamped to create an airtight system for the filters to soak in. Note that this method of pushing solutions through the filters means that none of the theorized surface tension problems discussed earlier will have effect here. Syringes were also used to pass deionized water and air through the filters during the rinsing and drying stages respectively.

Figure 18: Experimental setup for depositing Co nanoparticles within the syringe filters

Figure 19, below shows an example of a syringe filter with cobalt deposited inside. The cobalt is evidenced by the dark gray/black colored areas.

Figure 19: Syringe filter with cobalt (dark gray/black areas) deposited within

4.1.2 Measuring the Amount of Hydrogen Gas Generated

The process used for measuring the amount of hydrogen generated by the cobalt deposited on syringe filter catalyst structure is similar to the one used for the Co-nanoPPX (See 2.1.2 Measuring the Amount of Hydrogen Gas Generated). It utilizes the same concept of gas displacement of water. However, given the physical structure of the syringe filter, a new setup (See Figure 20) was needed for the hydrogen generation part of the system.
A T-junction was created using PDMS and the syringe filter was attached. The T-junction allowed for NaBH₄ solution to be continually passed through the filter while also allowing the resulting H₂ gas generated to pass up and through the attached plastic tubing into the volumetric glass tube where it displaced water. Two syringes were attached on both sides of the T-junction – one attached to the filter itself and one attached to the other side of the T-junction through plastic tubing – and were used to pull the NaBH₄ solution through the syringe filter continuously while maintaining a closed system. Polyethylene was used to help keep the system airtight. Figure 21 shows a close-up view of hydrogen gas being generated with this catalyst structure.
4.2 Results and Analysis

Figure 22, Figure 23, and Figure 24 respectively show the volume of hydrogen generated versus time for cobalt bath times of 1 minute, 2.5 minute, and 5 minutes. Using an assumed diameter of the inside filter membrane of 2.5 cm, the total area of the catalyst structure was calculated to be 4.91 cm\(^2\). Note that the cobalt catalyst most likely covers the majority of the syringe filter's insides, not just the filter membrane itself. Therefore, the calculated 4.91 cm\(^2\) area is actually a very rough estimate and will result in calculated hydrogen generation rates much higher than in reality. However, since the process for calculating the rates were consistent for all samples, general relationships should still be observable. The hydrogen generation rates calculated for the 1 minute, 2.5 minute, and 5 minute samples were respectively 0.5640 mL(min\(\cdot\)cm\(^2\))\(^{-1}\), 0.7022 mL(min\(\cdot\)cm\(^2\))\(^{-1}\), and 0.6015 mL(min\(\cdot\)cm\(^2\))\(^{-1}\).

![Image: Hydrogen Generation Rate: 0.5640 mL/(min•cm\(^2\))](image)

\[ y = 2.769x + 0.9333 \]
\[ R^2 = 0.9825 \]

Figure 22: H\(_2\) generated using cobalt on syringe filter (1 minute) sample
Figure 23: \(\text{H}_2\) generated using cobalt on syringe filter (2.5 minute) sample

\[
\text{Volume Hydrogen Generated (mL)}
\]

\[
4.91 \text{ cm}^2 \text{ total area}
\]

\[
\text{Hydrogen Generation Rate: } 0.7022 \text{ mL/(min} \cdot \text{cm}^2)\]

\[
y = 3.4479x - 1.6455
R^2 = 0.985
\]

Figure 24: \(\text{H}_2\) generated using cobalt on syringe filter (5 minute) sample

\[
\text{Volume Hydrogen Generated (mL)}
\]

\[
4.91 \text{ cm}^2 \text{ total area}
\]

\[
\text{Hydrogen Generation Rate: } 0.6015 \text{ mL/(min} \cdot \text{cm}^2)\]

\[
y = 2.9536x + 0.5318
R^2 = 0.9918
\]
Of particular interest is the fact that the rate decreased from $0.7022 \text{ mL}\,(\text{min}\cdot\text{cm}^2)^{-1}$ to $0.6015 \text{ mL}\,(\text{min}\cdot\text{cm}^2)^{-1}$ when the cobalt bath time for the last rate (5 minute) was twice that of the previous (2.5 minute). A likely explanation for this decrease in rate could be that the H$_2$ gas was not leaving the syringe filter fast enough during that particular experiment. If the H$_2$ gas does not move away from the Co catalyst, then the NaBH$_4$ solution is blocked from coming into contact with the catalyst. Thus no new H$_2$ gas can be generated from the NaBH$_4$ solution.

Another explanation could be that the longer cobalt bath time led to too much cobalt being deposited around the pores of the filter, causing them to become “clogged.” This would slow the progression of H$_2$ gas through the filter, which would again lead to the H$_2$ gas blocking off the cobalt catalyst from coming into contact with the NaBH$_4$ solution. During experiments, it was often observed that the H$_2$ gas traveled backwards out of the filter and into the syringe that was feeding the NaBH$_4$ solution into the filter. This observation gives credence to the idea that too much cobalt was deposited resulting in the pores of the filter being clogged.

In any case, these hydrogen generation rates, along with the possibility of being able to easily recirculate NaBH$_4$ solution through the catalyst structure, makes the cobalt syringe filter catalyst structure promising enough for future study.
5 Conclusions and Recommendations for Future Work

In summary, this thesis focused on developing an inexpensive means of extracting hydrogen gas from NaBH$_4$ solution by using nanotextured cobalt catalyst structures. Reduction in costs is possible not only through the replacement of noble metal catalysts with cobalt, but also from the easy scale-up capability of the catalyst fabrication process [6]. Hydrogen discharge rates comparable to those found in literature were obtained for each of the three sets of samples, with the highest discharge rate corresponding to the cobalt on syringe filter catalyst structures. Although, none of the catalyst samples’ hydrogen generation rates was enough individually to match the DOE targeted discharge rate of 0.02 g(H$_2$)/s (see Table 1), increasing the geometric area of the catalyst to about 7.32 m$^2$ (using an average H$_2$ generation rate of 0.2 mL/(min•cm$^2$)) would meet that goal (See Appendix for calculation). This could be accomplished by stacking the Co-nanoPPX or Co on polycarbonate membrane samples on top of each other, while insuring that there is enough space for fluid to pass through each layer. While 7.32 m$^2$ seems quite large, each “layer” of these catalyst structures is only microns thick. Therefore, the total unit “volume” would actually not be too cumbersome for practical applications.

In terms of future work, it might be interesting to investigate using ammonia borane (AB) fuel instead of NaBH$_4$ solution. AB is an appealing chemical hydrogen storage medium because of its high gravimetric capacity of H$_2$ (19.6 weight percent) and low molecular mass (30.7 g/mol) [3, 20]. Recent research has also shown that AB spent fuel can be inexpensively regenerated back to AB through a 24-hour treatment with hydrazine in liquid ammonia at 40°C in a sealed pressure vessel [20]. This would solve one of the main cost issues associated with the chemical hydrogen storage system.
It might also be interesting to conduct research into using these nanotextured catalyst structures with direct borohydride fuel cells instead of PEM fuel cells. Direct borohydride fuel cells skip the hydrogen gas production step and feed the sodium borohydride solution directly to the fuel cell. Equation 5 describes this reaction which has an equilibrium voltage of about 1.6V [21].

\[ BH_4^- + 2O_2 \leftrightarrow BO_2^- + 2H_2O + electricity \] (5)
Appendix

Calculating the cost of NaBH₄ in comparison to gasoline

The molar masses of NaBH₄ and H₂ are respectively 0.03783 kg/mol and 0.0020158 kg/mol. Therefore, given the reaction in Equation 3 and that 1 kg of NaBH₄ costs $55, the cost of producing 1 kg of H₂ is about $258, as shown in Equation 6 below. Taking into account reports of technology being developed that will reduce the cost to 1/10th of its current price, 1 kg of H₂ will cost about $25.80 to produce.

\[
\text{Cost of } H_2 = \left( \frac{\$55}{\text{kg NaBH}_4} \right) \times \left( \frac{0.03783 \text{ kg NaBH}_4}{1 \text{ mol NaBH}_4} \right) \times \left( \frac{1 \text{ mol NaBH}_4}{4 \text{ mol } H_2} \right) \times \left( \frac{1 \text{ mol } H_2}{0.0020158 \text{ kg } H_2} \right) \approx \frac{\$258}{\text{kg } H_2} \tag{6}
\]

\[
1/10 \text{ of current price to produce } H_2 = \frac{1}{10} \times \frac{\$258}{\text{kg } H_2} = \frac{\$25.80}{\text{kg } H_2} \tag{7}
\]

Since 1 kg H₂ is equivalent to 1 gallon of gasoline and gasoline currently costs on average about $4 per gallon, the NaBH₄ storage system is 6.45 times more expensive.

\[
H_2: \text{gasoline cost ratio} = \left( \frac{\$25.80}{1 \text{ kg } H_2} \right) \times \left( \frac{1 \text{ kg } H_2}{1 \text{ gallon gasoline}} \right) \times \left( \frac{1 \text{ gallon gasoline}}{\$4.00} \right) = 6.45 \tag{8}
\]

Calculating Hydrogen Generation Rates

The rate of H₂ generation for each sample was calculated by first plotting the Volume of Hydrogen Generated (mL) versus Time (minutes). Using a linear regression model to fit the data points, the rate in mL/min of H₂ gas being generated is estimated to equal the slope of the linear model. To take into consideration the amount of catalyst being used to produce this...
rate, the rate is then divided by either the total area covered by the catalyst or the total weight of catalyst deposited over this area. For example, the rate of H₂ gas generated for the Co-nanoPPX sample was determined from the plot to equal 1.0397 mL/min. Since the total area covered by the catalyst is of 4.6875 cm² and the total weight of the cobalt deposited over this area is about 0.0026 grams, the rates are respectively 0.2214 mL/(min•cm²) and 392.7189 mL/(min•g(\text{Co})).

\[
\text{Rate in terms of area covered by catalyst} = \left( \frac{1.0397 \text{ mL}}{\text{min}} \right) \times \left( \frac{1}{4.6875 \text{ cm}^2} \right) = \frac{0.2214 \text{ mL}}{\text{min} \cdot \text{cm}^2} \quad (9)
\]

\[
\text{Rate in terms of weight of Co deposited} = \left( \frac{1.0397 \text{ mL}}{\text{min}} \right) \times \left( \frac{1}{0.0026 \text{ g}} \right) = \frac{392.7189 \text{ mL}}{\text{min} \cdot \text{g(\text{Co})}} \quad (10)
\]

**Calculation of the total catalyst area needed to meet DOE targets**

The DOE target discharge rate is 0.02 g(H₂)/s. The density of H₂ at room temperature is 0.082 g/L. Therefore, assuming that the average rate of H₂ generated for the Co-nanoPPX and cobalt on polycarbonate membrane catalyst structures is about 0.2 mL/(min•cm²)⁻¹, the geometric area of catalyst needed is about 7.32 m².

\[
\text{Area needed} = \left( \frac{0.02 \text{ g H}_2}{\text{s}} \right) \times \left( \frac{1000 \text{ mL H}_2}{0.082 \text{ g H}_2} \right) \times \left( \frac{\text{min} \cdot \text{cm}^2}{0.2 \text{ mL H}_2} \right) \times \left( \frac{60 \text{ s} \cdot \text{m}^2}{\text{min} \cdot 100^2 \text{cm}^2} \right) = 7.32 \text{ m}^2 \quad (11)
\]
References


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Research Internship in Science & Engineering, Univ. of Duisburg-Essen, Germany
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