INCREASING FUEL CELL RUN TIME BY PREVENTING PRECIPITATION OF REACTANTS OR PRODUCTS IN DIRECT SODIUM BOROHYDRIDE FUEL CELL

BY
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THESIS
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This work aims to maximize usable run time of direct sodium borohydride / hydrogen peroxide (NaBH₄ / H₂O₂ ) proton exchange membrane fuel cell, given a fixed volume of fuel solution. In the fuel cell being developed here at the University of Illinois, there is a need to manage water flow so as to avoid reaching solubility limits of reactants as well as products, which dominate the fuel cell run time. The model for solubility is built on solubility product and common ion effect theory. Hence, the model not only considers the decrease of water in the solution but also considers the effect on solubility limit of both reactant and product due to dynamic formation of NaBO₂, utilization of NaBH₄ and presence of NaOH; which is used to stabilize the NaBH₄ solution to keep it from producing H₂ gas. A voltage current model has also being incorporated to enhance our model by studying variation in voltage and current with time and reflecting back the values for realistic run time calculation for constant power usage. Our model predicts an improvement in fuel cell run time with optimum water addition. This would require additional water management schemes as discussed in the work.
To my parents and teachers
ACKNOWLEDGMENTS

I would like to start with thanking Prof G H Miley, who was more than just an advisor to me, he was my guide, my mentor, guiding me through out my academic progress at the University of Illinois. He showed me the right way whenever I got lost in my research as well as life. I also thank Dr Luo, Dr Kim and Dr Yang, who work with Prof Miley, for their valuable inputs in this thesis and my research work in general. I sincerely thank all those who have had their valuable feedback during presentations at ASME 8th international fuel cell conference, June 2010, NY and Fuel cell seminar, Nov 09, Palm Springs, Ca.

I am indebted to the Department of Aerospace engineering for the intellectual enhancement I have had in past 2 years, with the courses and interactions with faculty members and fellow students. These in turn empowered me with the tools to succeed in my research work and am sure will stay with me forever. I am grateful for the travel grant with which I have been able to attend conferences and present my work, which is a part of this thesis. My thanks to all the staff of Aerospace department, with special mention for Ms Staci Tankersley, who made my transition to this program easy and guided me on numerous aspects, right from college formalities to funding opportunities through out the program. She has been a great graduate coordinator.
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Nomenclature

$E_{\text{Thermo}}$ = Theoretical voltage

$E_0$ = standard cell potential at the temperature of interest

$R$ = Universal gas constant

$T$ = Temperature

$n$ = number of electrons transferred in cell reaction

$f$ = Faraday constant

[products] = activity (concentration in liquid) of products

[reactants] = activity (concentration in liquid) of reactants

$\Delta G$ = Gibbs free energy

$j$ = current density

$j_0$ = exchange current

$\alpha$ = transfer coefficient

$\eta_{\text{act}}$ = activation voltage loss

$\text{ASR}_d$ = Area specific resistance of diffusion

$\text{ASR}_m$ = Area specific resistance of membrane

$\eta_{\text{ohm}}$ = ohmic voltage loss

$L$ = length of the conductor

$A$ = Area

$\sigma$ = Conductivity

$j_L$ = limiting current density
Chapter 1. Introduction

Fuel cell is an electrochemical conversion cell, generally with a capability to refill or provide continuous supply of fuel (Hydrogen source). These have wide application as a power source for automotive, stationary generators, portable devices, aerospace propulsion, underwater applications etc. In simple terms, it consists of a hydrogen source and oxygen separated by a membrane. In proton exchange membrane fuel cells, the hydrogen molecule gets converted to proton and passes through the membrane to react with oxygen to give water. The electron is transferred through an external circuit, giving rise to a current.

![Fuel cell schema](image)

**Figure 1.1 Fuel cell schema**

Fuel cell has had strong links to space programs with first commercially available fuel cell as a part of Project Gemini. At University of Illinois, our group is developing an oxygen free Sodium borohydride - hydrogen peroxide fuel cell, aimed at underwater and space applications. This system can provide high energy density,
which compliments the purpose of space applications. Fuel cell technology also helps achieve environment challenges posed by competing technologies like lead acid batteries as the product NaBO$_2$ is environment friendly [1].

1.1 Sodium Borohydride- Hydrogen peroxide fuel cell

Chemical Hydrides, owing to their high hydrogen content are alternative solutions for Hydrogen storage. Our system (DBFC) uses NaBH$_4$ solution, directly in our fuel cell, aiming to minimize losses due to external H$_2$ generation.

On the cathode side H$_2$O$_2$ is used as an oxidant. The reactions are as shown:

Anode Reaction: $\text{NaBH}_4 + 4\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 8\text{H}^+ + 8\text{e}^-$

Cathode Reaction: $4\text{H}_2\text{O}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow 8\text{H}_2\text{O}$

The solution consisting of NaBH$_4$ is alkaline to prevent unanalyzed hydrolysis. Experimental results have indicated a current density of 250mA/cm$^2$ and a power density around 1.5 W/cm$^2$ power density [3]. Other studies [10] have shown a lower value of 0.6 W/cm$^2$, but were published earlier than [3] which presented improved catalyst performance.

Compact all-liquid generation ensures quick start up and functioning in oxygen free environment which is optimum for space applications.
In general the solubility limit of any chemical in weight of solvent is measured in a volumetric unit (usually liter) of the solution. But this is dependent on factors such as temperature, solution and presence of other solvents. To avoid the effect of other solvents and to standardize solubility across chemicals their solubility product is defined. For ionic solvents it is defined as the product of number of ions (activity in
non-ionic case) per liter of the solution. In our case NaBH$_4$ ionizes to [Na$^+$] and [BH$_4$]$^-$, hence the solubility product (Ksp) is given by

\[ \text{Ksp} = [\text{Na}^+][\text{BH}_4^-] \]

where [Na$^+$] and [BH$_4$]$^-$ are in moles per liter of water.

The above definition is derived from the ionization reaction:

\[ \text{NaBH}_4 (s) \rightarrow \text{Na}^+(\text{aq}) + \text{BH}_4^- (\text{aq}) \]

NaBH$_4$ being a pure solid is not included in equilibrium expression. This gives the idea of solubility, where more addition of solvent doesn't affect the ionization as both dissolving and reforming balance each other. This also shows that increasing the surface area by powdering or stirring does not shift the equilibrium or Ksp, it just speeds up the attainment of equilibrium.

**Common Ion Effect**

The most important advantage of using Ksp over weight/liter is that it accounts for the common ion effect. Solubility of a salt is affected by presence of other salts, containing similar ions. The presence of common ions, as the name suggests, decreases the solubility limit of the salt. For instance, in our solution NaOH is present, which is present as Na$^+$ and OH$^-$ ions, thus making the solution alkaline.

As mentioned earlier, the addition of NaOH decreases the evolution of H$_2$ gas when NaBH$_4$ is added to the solution. But the common ion [Na$^+$] decreases the solubility
of both reactant/fuel NaBH₄ as well as product NaBO₂. As Na⁺ ions are already present in the solution even before adding the solvents.

1.3 Previous work

Usually fuel water management in PEM fuel cells is due to scarcity of water to wet the fuel cell membrane, which drastically reduces membrane performance thereby increasing ion transfer resistance [7]. As our fuel cell is an all liquid fuel cell, a different kind of challenge is presented where fuel cell run time is reduced due to precipitation of fuel or reaction products. Scott et al had worked on this specific issue in their model [4]. Their model assumed constant current and voltage for the fuel cell and calculated the solubility by weight of both reactants and products. When the solubility limit was reached, the fuel cell stopped running. Run time of a fuel cell is defined as the maximum time the fuel cell can operate for a given quantity of fuel delivering constant power and satisfactory voltage (Voltage below 30% of the rated voltage is deemed to be under performance). This model also did not consider effect of other chemicals in the solution. As discussed earlier the actual solubility is lower than rated solubility in presence of other chemicals sharing the common ion. Also the assumption of constant current and constant voltage introduces uncertainty in the run time value.

Solubility product is used as an indicator of solubility to solve the problem mentioned above with the solubility limit by weight. Voltage-current model is also introduced to map the voltage and corresponding current value and to improve the model.
1.4 Objective

The objective of this work is to improve the run time of the fuel cell by optimizing water addition to prevent precipitation of the fuel or the product. So given a fixed amount of fuel, it is desired to ensure maximum fuel utilization by avoiding precipitation. Fuel utilization is defined as the amount of fuel used up divided by the amount of initial fuel supplied. It can also be posed as minimizing the fuel left in the solution, when the fuel cell stops working. Precipitation, as experimentally seen, clogs the fuel cell channels and deposition on catalyst layer effects the overall fuel cell resistance thereby causing a drop in the performance [11]. Water addition rate needs to be optimized to avoid any additional non-performing weight, as weight is an important criteria for its application domain. The goal is to improve run time by maximizing fuel utilization. Fuel cell also stops running when voltage drops below usable level. For our case, the voltage drop should not be lower than 30% of the rated voltage.
Chapter 2. Description of the Model

As mentioned in our objective, we aim to prevent precipitation of either H₂ source (NaBH₄) or product (NaBO₄) in the anode of our all-liquid fuel cell. As water is used up in the hydrogen generating reaction, there is an increase in fuel concentration with time. The precipitation of solvents affects the permeability of diffusion layer.

Anode: \[ \text{NaBH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 8 \text{H}^+ + 8 \text{e}^- \]

Our model calculates solubility product of the solvents and helps in deciding on the optimum water addition rate required to prevent precipitation. To do so, there are two modules in our model – the solubility module and the voltage-current module. At each time step the code checks if the solution has reached the solubility limit and if it has not, it moves to the voltage-current module to calculate the predicted current with change in voltage for the next time step. Algorithm for the model is as shown in figure 2.1.

Figure 2.1 Algorithm for the Computational model
2.1 Solubility Module

The model works on the basis of calculation of the solubility product. NaOH is generally added to the solution to stabilize NaBH₄ in water and prevent undesired reactions (evolution of H₂). Due to the presence of Na⁺ ions from NaOH and NaBH₄, precipitation of solvent happens even before the individual solubility limit is reached, as explained by the common ion effect.

Solubility limit for NaBH₄ in H₂O is 46.9% by weight at 60°C. Hence, the number of moles in 100g of H₂O (100 ml) is 46.9/37.82 = 1.2400.

As NaBH₄ ionizes completely in the water solution, solubility product limit is calculated as follows:

\[ K_{sp} = [Na^+] [BH_4^-] = 153.78 \]

Similarly solubility product for NaBO₂ is calculated to be 15.6 (given 26% by weight at 60°C). This value signifies the number of moles needed to precipitate solute based on each ions in one liter of water.

Presence of an other source of Na⁺ ion, affects the amount of NaBH₄ or NaBO₂ needed to precipitate in given solution. This theory is further validated by the observations presented in model validation chapter.

The model starts with an assumed current of 5 A and a voltage of 0.5 V. These parameters will change with time steps and get to the best possible working
configurations determined by the model, keeping a constant power of 2.5 Watts. Now, within each time step the current is constant which gives an indication of the amount of fuel utilized for the generation of electrons. With charge balance, the amount of product formed and water utilized in the reaction is determined. One more factor is considered in the change in water quantity; which is the diffusion of water from anode to cathode and vice versa. An experiment was carried out in [9] to study the net effective H₂O drag minus back diffusion. This parameter was found to be 4.36 at 60°C for Nafion 112 membrane.

![Diagram of water transport across membrane](image)

**Figure 2.2: Water transport across membrane**

The model then calculates $K_{sp}$ for NABH₄ and NaBO₂ with the available amount of each ion in the remaining quantity of water. This model then connects to the voltage-current module to determine the effect of change in concentration of reactants and products on
the change in current and voltage. The voltage-current module is described in the next section.

2.2 Voltage-current module

In majority of applications it is desired to have the fuel cell deliver a constant power output. But as the reaction proceeds, there is a drop in concentration of the fuel along with other associated losses. The model for voltage-current predicts voltage for a given current, and it boosts up current with the drop in voltage to deliver constant power. In real situations external compensatory circuit / systems are present for this purpose. Voltage-current model basically establishes the difference between actual voltage and theoretical voltage and the losses attributed to reaction kinetics, charge transport and mass transport.

\[ V = E_{\text{thermo}} - V_{\text{act}} - V_{\text{ohmic}} - V_{\text{ionic}} \]

This work was done previously by [7]. But, it has been significantly modified to match the fuel cell specifications mentioned in this study. At each step the model calculate the change in voltage and adjusts the current to maintain a constant power. (VI=constant)

1) \( E_{\text{Thermo}} \)

This is the voltage, the fuel cell would give if there were no losses involved. It is mainly given by the Nernst Equation, which has 2 parts, namely \( E_0 \) - thermodynamically calculated potential and other, which relates chemical potential to concentrations through activity.
\[ E_{\text{thermo}} = E_0 - \frac{RT}{nf} \ln \left( \frac{\text{[products]}}{\text{[reactants]}} \right) \]

where, 

- \( E_0 \) = standard cell potential at the temperature of interest
- \( R \) = Universal gas constant
- \( T \) = Temperature
- \( n \) = number of electrons transferred in cell reaction
- \( f \) = Faraday constant
- \([\text{products}]\) = activity (concentration in liquid) of products
- \([\text{reactants}]\) = activity (concentration in liquid) of reactants

\( E_0 \) can be calculated from Gibbs free energy of the reactants given by:

\[ E_0 = -\frac{\Delta G_f}{n^*f} \]

where,

\[ \Delta G_f = \Delta G_{\text{products}} - \Delta G_{\text{reactants}} \]

Anode Reaction:  \( \text{NaBH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 8 \text{H}^+ + 8 \text{e}^- \)

Cathode reaction:  \( \text{H}_2\text{O}_2 + 2 \text{e}^- \rightarrow 2 \text{OH}^- \)

\( \text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} \)

Overall Reaction:  \( \text{NaBH}_4 + 4 \text{H}_2\text{O}_2 \rightarrow \text{NaBO}_2 + 6 \text{H}_2\text{O} \)
Now, ΔG from the Gibbs free energy of formation of each individual compounds is as given in the table 2.1

<table>
<thead>
<tr>
<th>Molecules</th>
<th>ΔG_f (kJ/mol)</th>
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<tbody>
<tr>
<td>BH_4</td>
<td>114.4</td>
</tr>
<tr>
<td>H_2O_2</td>
<td>-120.4</td>
</tr>
<tr>
<td>BO_2</td>
<td>-678.9</td>
</tr>
<tr>
<td>H_2O</td>
<td>-237.1</td>
</tr>
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</table>

**Table 2.1: Gibbs free energy [5]**

ΔG is found to be 1729 KJ, from which we have

\[ E_0 = \frac{1729\times1000}{(8\times96485)} = 2.240 \text{ V.} \]

Effect of activity of reactants and products is also to be considered in the model. As it is an all liquid fuel cell and all the involved elements are stable in water, we can consider concentrations to be representative of activity.

\[ E_{thermo} = E_0 - \frac{RT}{nf} \ln\left(\frac{[NaBO_2]}{[NaBH_4][H_2O_2]^t}\right) \]

Note that the activity of water is 1 as it is the solvent.
2.2.1 Activation Loss

The rate of reaction depends on the probability of reactants crossing the activation energy. The loss of voltage associated with reaction rate is termed as activation loss. At low current densities, this is the main source of loss. Butler-Volmer equation is used to relate between current densities with the activation voltage.

Net current density, \( j \), is given by (forward – reverse activation barrier)

\[
j = j_0 \left( e^{\alpha n F \eta_{ac}/RT} - e^{-(1-\alpha)n F \eta_{ac}/RT} \right)
\]

Where \( j \) = current density

\( j_0 \) = exchange current

\( \alpha \) = transfer coefficient

\( \eta_{ac} \) = activation voltage loss

A simplified version of the above equation will be used. Given a large \( \eta_{ac} \) (50-100 mv), it is practical to neglect the \( e^{-\text{large}} \) term, Hence;

\[
\eta_{ac} = -\frac{RT}{\alpha NF} \ln(j_0) + \frac{RT}{\alpha NF} \ln(j)
\]

Or

\[
\eta_{ac} = a + b \ln(j)
\]

This is also called the Tafel Equation.

The parameters for the above equation have been obtained in [9] and have been used in [7]. They have also been verified by matching the results with the experimental curve. The values have been tabulated in table 2.3.
Considering loss in both electrodes,

\[ \eta_{act} = (a_a + b_a \ln(j)) + (a_c + b_c \ln(j)) \]

<table>
<thead>
<tr>
<th>Parameter names</th>
<th>Values</th>
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<tr>
<td>(a_A)</td>
<td>0.066V</td>
</tr>
<tr>
<td>(b_A)</td>
<td>0.007V</td>
</tr>
<tr>
<td>(a_C)</td>
<td>0.037V</td>
</tr>
<tr>
<td>(b_C)</td>
<td>0.008V</td>
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Table 2.2 Parameters for Activation loss

### 2.2.2 Ohmic Loss

This is the loss due to the movement of ions/electrons through the diffusion layer and Nafion membrane. Diffusion layer consists of the catalyst deposited on a carbon cloth. Ions travel through the electrolyte in the porous channels of the cloth.

\[ \eta_{ohmic} = j^* [ASR_d + ASR_m] \]

where, \(ASR_d\) = Area specific resistance of diffusion

\(ASR_m\) = Area specific resistance of membrane

ASR is area multiplied by the ohmic resistance of the layer.

Resistance is given by \(R = \frac{L}{A \sigma}\)

where, \(L\) = length of the conductor

\(A\) = Area
\[ \sigma = \text{Conductivity} \]

Therefore, \( \text{ASR} = A^*R = L/\sigma \)

Substituting, we get,

\[ \eta_{\text{ohmic}} = j \ast \left[ \frac{l_d}{\sigma_d} + \frac{l_m}{\sigma_m} \right] \]

For Nafion membrane,

\[ L_m = 0.0051 \text{ cm} \]
\[ \sigma_m = 0.15 \text{ S/cm} \quad [9] \]

\[ L_d = 0.005 \text{ cm is half the actual width as separated in [6]. Conductivity } \sigma_d \text{ is guessed at 3 mS/cm since it is an ionic solution.} \]

### 2.2.3 Concentration Loss

This loss in performance is mainly because of reactant depletion within the catalyst layer and can be lowered by improving mass transport in electrodes and diffusion layer.

This is because of two reasons:

a) Nernstian loss as given in Nernst equation and

b) Reaction losses which are due to reduced concentration near the catalyst.

Limiting current is also a concern as it is the maximum current possible by reaction, above which the reactant concentration falls to zero at the catalyst.

\[ \eta_{\text{conc}} \] is given by
\[ \eta_{conc} = \frac{RT}{nf} (1 + \frac{1}{\alpha}) \ln\left(\frac{j_L}{J_L - j}\right) \]

where, \( j_L \) = limiting current density.

The limiting current density is assumed to be 2 A/cm\(^2\), which is within reasonable limits as mentioned in [12]. This can also be seen in the experimental plots obtained.

Apart from the aforementioned parameters, one more factor dominates the losses. Leakage current, \( j_{\text{leak}} \), is defined as the current which does not flow through the desired external circuit. This affects all the above losses except Ohmic loss, as this does not add to the voltage loss due to resistance. The effect of leakage current is to shift the voltage current curve leftwards. This can be found by the shift in the experimental and model output. For the experimental fit, leakage current is assumed to be 0.9 A/cm\(^2\).

The whole equation modifies to,

\[ V = E_{\text{thermo}} - \eta_{act}(j + j_{\text{leak}}) - \eta_{\text{ohm}}(j) - \eta_{\text{conc}}(j + j_{\text{leak}}) \]
Chapter 3. Model Validation

As mentioned in the model description, the model is divided into two modules voltage-current(VI) module and solubility module .This chapter examines each of these modules individually and validate/improve the output with the experimental values. Validation is an important aspect of simulation studies and validating each module helps us incorporate losses, which might have been missed by the model.

3.1 Voltage current model

We run the voltage current (VI) module and plot the effect of change in current density on voltage output of the fuel cell. This is important as it helps us to map the current drawn corresponding to the voltage delivered, hence helps us to determine the amount of fuel used up in a given time step. Each of the losses have been explained in chapter two. For the following figure generated from the model, the open circuit voltage [current density \( j = 0 \) ] is 2.24 V. It is to be noted that there is leakage current even in the case of an open circuit.

**Activation loss:**

In figure 3.1, it is seen that activation loss is mainly dominant at lower current densities as at higher current densities other losses play a major role.

![Figure 3.1 Activation loss](image)
Concentration loss:

Concentration loss is due to the drop in concentration at higher current densities, when there is a local starvation of fuel due to high rate of reaction to generate high currents. This is shown in Figure 3.2.

Ohmic loss:

As expected, it shows a linear relationship between current density and voltage drop. For a single cell of 25 cm$^2$ the voltage drops from 2.24 V to 2.04 volts due to ohmic losses in the cathode and anode.

All the above figures, with individual losses, reflect the trend as defined in [12]

Voltage-Current plot:

After combining all losses and plotting it against various values of current density, figure 3.5 is obtained. Note that the x-axis is not current density, but current to facilitate comparison with the experimental observation. As mentioned before, $j_{\text{leak}}$ accounts for the shift in the voltage current curve to fit the voltage current curve.
Experimental studies described in another paper from our lab [3] show that the V I curve for the model and the experiment nearly match each other. We use a normalization factor (57.9842 [6]) for concentration loss to fit the curve for higher currents. The above graph was obtained for 25 cm² fuel cell and hence current densities match in the range mentioned above. One thing to be observed here is that for 2.5 W power output, the voltage-current curve configuration is for voltages around 1.7 V and current around 1.5
A. This is an important note; as it reflects how our system would behave to give a power output of 2.5 W for this fuel cell.

3.2 Solubility limit Module:

To validate the solubility limit module, there is a need to experimentally verify the drop in solubility of fuel/product with the presence of the common ion. Experiments were conducted at room temperature, where solubility (by weight) was measured for 2 different concentrations of Sodium hydroxide. The solubility limit by weight of sodium borohydride was found out to be 21.9 g in 50 ml of water solution with 10% of NaOH by weight. This corresponds to 43.8% by weight. In order to theoretically predict the solubility limit for Sodium borohydride in 10% Sodium hydroxide solution by the table 3.1 is used and associated calculation is performed.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>% By weight in water solution</th>
<th>Amount in 1000ml of water</th>
<th>Molecular weight g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>10</td>
<td>100</td>
<td>40</td>
</tr>
<tr>
<td>NaBH4</td>
<td>?</td>
<td>X</td>
<td>37.8</td>
</tr>
</tbody>
</table>

Table 3.1 Data to calculate the weight percent of the Solute

The Solubility product at precipitation for Sodium borohydride is 154. Hence, in 1000 ml of water, product of the number of moles of sodium and borohydride ion is 154.

\[ K_{sp} = 154 = [Na^+] [BH4^-] \]
This means there is 424.2 g in 1000 g of solution. Hence, the solubility by weight is 42.4 %. A considerable difference is present as compared to the solubility limit without the NaOH, around 47% by weight.

Similarly, calculations were performed for 30 % Sodium hydroxide solution and it was found that the solubility limit further drops to 34.8 % by weight. Other sources have reported similar trend and values. The difference is mainly due to experimental inaccuracy.

Figure 3.6 Solubility of NaBH4 [2]
In figure 3.6, for the 10% NaOH curve, there is a sudden increase in the solubility limit from room temperature to 60°C. And, at 60°C there is a considerable variation in sodium borohydride solubility limit with different concentrations of NaOH.
Chapter 4. Model Results

After the model has been validated, our objective now is to increase the run time. For comparison, a limited quantity of fuel (500 g fuel solution) is assumed. It is again emphasized that water is used up in the reaction due to which the precipitation of reactant/products takes place, thereby drastically reducing the fuel cell run time. The solubility of sodium borohydride in plain water solution is 47% and product sodium metaborate is 26%. The following figure shows the result from Scotts paper [4], without considering the effect of sodium hydroxide in the solution. W Hr is used as the measure of run time, given that the fuel cell output is measured by the time it could provide X watts of energy. This provides a uniform platform to compare different initial concentrations.

Figure 4.1 Weight percent v/s time - 10 Wt%
This basically shows that NaBO$_2$ would start precipitating at 57 W-Hr, thus limiting fuel cell run time. Actual precipitation occurs even before this point is reached. The above graph is for an initial concentration of 10% by weight NaBH$_4$ solution at 60°C ($\lambda = 4.36$, $I = 5$ A, $V = 0.5$ V).

Solubility limit of NaBH$_4$ is not a bottleneck for this configuration, but could be an important consideration for higher initial concentrations of NaBH$_4$. It is important to consider a higher concentration for a higher run time range usage.

Our solubility model, as explained, is not based on weight but on solubility product and hence, the common ion effect is used to consider effect of different solvents in the solutions.

<table>
<thead>
<tr>
<th>Molar solution</th>
<th>% by weight</th>
<th>Run time W Hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.4</td>
<td>70.66</td>
</tr>
<tr>
<td>0.25</td>
<td>1</td>
<td>70.2083</td>
</tr>
<tr>
<td>0.5</td>
<td>2</td>
<td>69.42</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>67.875</td>
</tr>
<tr>
<td>1.5</td>
<td>6</td>
<td>66.42</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>65</td>
</tr>
<tr>
<td>2.5</td>
<td>10</td>
<td>63.66</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>57.667</td>
</tr>
</tbody>
</table>

*Table 4.1 Runtime for different concentration of NaOH*

Table 4.1 shows that lower that the concentration of NaOH, more time it takes for precipitation of NaBH$_4$/NaBO$_2$. But something that this model does not include is the fact
that if the solution is not alkaline, NaBH\textsubscript{4} is not stable in water solution and results in evolution of hydrogen gas. Thus, for the model it is safe to consider 4\% by weight \cite{13} of NaOH, i.e 1 molar solution in the study.

![Figure 4.2 Solubility product – without VI model](image)

As shown above, run time, as defined by precipitation of fuel, is 67.875 W-Hr. This is mainly because different solvents in the solution affect each other’s solubility limit. But still there is still an issue unaddressed in above model, which is the drop in voltage. Usually, drop in output voltage is an important factor in any power source, as the applications it is connected to generally are rated for certain designed voltage range. Power sources usually have inbuilt mechanisms to maintain output voltage constant. The algorithm for the voltage-current model is described in chapter 3. The fuel cell performance, solubility limit v/s energy output is shown in graph 4.3.

Contrary to our expectation, we see a further increase in the fuel cell run time to 230 W Hr. This is because of the fact that as mentioned in the voltage-current graph comparison
in model validation chapter, for 2.5 W, the output optimum configuration is at voltage of 1.7 V and a current around 1.5 A. This is automatically set in the model where it finds the optimal configuration for current and voltage. It is always possible to have an external control circuit to regulate the output and the fuel cell still delivers the desired constant power of 5W. Note that the water addition hasn’t being introduced yet, which is the main crux of improving the runtime. This will further discussed in chapter 5.

Figure 4.3 Solubility v/s time - with VI
Chapter 5. Fuel cell optimization

As mentioned in chapter 4, the fuel cell run for 229.5 W Hr. The main reason for the limited run time was precipitation of fuel solution. This can be avoided by addition of water. Water addition optimum is important as this is mainly intended to be used in space application where weight is most important criteria. Hence, maximum run time for given quantity of fuel is preferred.

5.1 Case 1: 10% Initial fuel concentration

Figure 5.1 shows the run time of 10% NaBH$_4$ fuel solution. This corresponds to 1.5275 moles of NaBH$_4$ in the solution. When the precipitation of NaBO$_2$ occurs, there is still 0.8949 moles of NaBH$_4$ unutilized. That means only 41.41% of NaBH$_4$ is utilized. There is no considerable decrease in voltage (fig 5.2), hence run time is considerably reduced by precipitation of reaction product just by precipitation of the product.

![Figure 5.1 Solubility product - 10%](image)
From fig 5.2, we can see that voltage fuel cell is operating around 1.7 V to deliver power output of 2.5 W. This is the best fuel cell configuration to deliver 2.5 W and if it is required to deliver larger currents/voltages for same power output, an external circuit transformer to boost the current can be installed. The voltage-current model ensures the fuel cell is operating at rated voltage and current as mapped in the voltage-current graph.

Table 5.1 shows how the fuel utilization changes with different rate of water addition. With water addition there is a considerable increase in the fuel utilization and thus the fuel cell run time.
<table>
<thead>
<tr>
<th>Sl No</th>
<th>Water addition rate (ml/min)</th>
<th>NaBH4 moles left</th>
<th>Fuel utilization %</th>
<th>W Hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.8949</td>
<td>41.41</td>
<td>229.5</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>0.8167</td>
<td>46.54</td>
<td>257.8333</td>
</tr>
<tr>
<td>3</td>
<td>0.02</td>
<td>0.7164</td>
<td>53.1</td>
<td>294.125</td>
</tr>
<tr>
<td>4</td>
<td>0.03</td>
<td>0.5833</td>
<td>58.33</td>
<td>342.2917</td>
</tr>
<tr>
<td>5</td>
<td>0.04</td>
<td>0.398</td>
<td>73.94</td>
<td>409.2917</td>
</tr>
<tr>
<td>6</td>
<td>0.05</td>
<td>0.1227</td>
<td>91.97</td>
<td>508.8333</td>
</tr>
<tr>
<td>7</td>
<td>0.053</td>
<td>0.012</td>
<td>99.21</td>
<td>548.333</td>
</tr>
</tbody>
</table>

Table 5.1 Effect of water addition – 10%

By adding 0.053 ml/min of water we were able to increase the fuel cell run time by 138.9% from 229.5 W Hr to 548.33 W Hr. Figure 5.3 shows the fuel utilization. We can see that at optimum water addition fuel utilization is nearly 100%, compared to 41% with no water addition. As noted earlier, the issue in this is precipitation of NaBO₂. Similar to the plot for fuel utilization, power output also increases with water addition, as we increase the fuel cell run time.

Figure 5.5 represents the plot for solubility with time. It can be seen that for optimum water addition, precipitation delayed till 100% fuel is utilized. One point to be noted is that as fuel quantity decreases, there is a decrease in the voltage. Hence, the fuel cell
might run at high current output to deliver rated power, which might not as desired in application design.

**Figure 5.4** Energy out for different water addition rate – 10%

**Figure 5.5** Solubility graph with optimum water addition – 10%
5.2 Case 2: 30% Initial fuel concentration

Similarly, it is also essential to look at a case where precipitation of NaBH₄ restricts the fuel cell run time. At higher concentrations, for example 30% NaBH₄ concentration, there is an issue with NaBH₄ solubility and not NaBO₂. Plot of solubility (Fig 5.6) shows the solubility product of solutes with respect to W Hr.

![Graph showing solubility product of solutes with respect to W Hr.](image)

Figure 5.6 Solubility – 30%

Run time is lower as compared to 10% initial concentration, which is because precipitation occurs faster due to higher concentration of NaBH₄. There is a low fuel utilization without water addition. Table 5.2 shows the change in fuel utilization and power output with water addition rate. A ten times increase in power output is predicted with increase in fuel utilization from 7% to 100%.
<table>
<thead>
<tr>
<th>Sl No</th>
<th>Water addition rate</th>
<th>NaBH4 moles left</th>
<th>Fuel utilization %</th>
<th>WHr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>5.4812</td>
<td>6.97</td>
<td>149.5417</td>
</tr>
<tr>
<td>2</td>
<td>0.025</td>
<td>5.3</td>
<td>10.04</td>
<td>215.375</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>5.0941</td>
<td>13.54</td>
<td>290.125</td>
</tr>
<tr>
<td>4</td>
<td>0.075</td>
<td>4.6698</td>
<td>20.74</td>
<td>444.0833</td>
</tr>
<tr>
<td>5</td>
<td>0.0875</td>
<td>4.22</td>
<td>28.22</td>
<td>603.9583</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>3.2952</td>
<td>44.07</td>
<td>942.125</td>
</tr>
<tr>
<td>7</td>
<td>0.125</td>
<td>0.0401</td>
<td>99.32</td>
<td>2119.4</td>
</tr>
</tbody>
</table>

Table 5.2 Effect of water addition – 30%

Figures 5.6 and 5.7 are graphical representation of the result presented in the table. Both fuel utilization and power output increases steeply with water addition. Optimum water addition for 100% fuel utilization is 0.1125 ml/min.

![fuel utilization graph](image)

Figure 5.7 Fuel utilization – 30%
Figure 5.8 Energy out with water addition – 30%

Figure 5.9 shows the effect of optimum water addition on solubility. With time, there is a decrease in concentration of the fuel, and precipitation of product happens exactly when the fuel is completely utilized.

Figure 5.9 Solubility with optimum water addition - 30%
5.3 Water source design

The above mentioned model presents an optimum water addition rate for the fuel cell to avoid precipitation. The simplest design solution is to provide external water source and a mechanism to periodically pump water into the solution. The model requires a constant water addition rate of 0.053ml/min to improve the run time. This would require an external tank of 698 ml for 500 ml 10% fuel initial concentration. This means an equal amount of storage space for water source is required, an important part of system design consideration.

Alternatively, water produced in the cathode can be circulated to the anode. Major challenge in this methodology is the separation of hydrogen peroxide and water. This is a completely a different research project. Various techniques like Anion exchange, electro osmosis or vacuum distillation can be used to felicitate the recirculation. These techniques need further investigation to avoid an undesired reaction in anode due to hydrogen peroxide.
Chapter 6. Conclusion and Future work

6.1 Conclusion

The objective of this thesis was to develop a model to calculate optimum water addition to increase the fuel cell run time. Solubility model based on solubility product and common ion theory has been used for our fuel cell model to determine precipitation. To improve accuracy of prediction of fuel utilization and fuel cell run time, voltage current and solubility models have been coupled. Apart from the above two scientific advancements, this thesis proposes a model which can predict fuel cell run time for a given initial fuel cell solution. The effect of different ions in the initial fuel cell solution on solubility of fuel and product have been incorporated in the solubility model via the use of solubility product and common ion effect theory. This model can be further used to determine optimum water addition rate to maximize fuel cell run time, for a limited quantity of fuel.

For 10 % initial concentration of Sodium borohydride, with 0.053 ml/min water addition rate, there is an increase of run time by 138 % (from 229.5 W Hr to 548.33 W Hr). This run time is achieved by running the fuel cell in optimum voltage-current configuration to deliver 5 W of power. If given a choice of adding an external water supply tank, this would require 698 ml to achieve maximum run time. The model presented can give a
relation between fuel precipitation and voltage current performance for any initial concentration of the fuel.

There were two important learning from this work. First the fact that with optimum water addition we could increase the fuel cell run time. Successful effort was made to actually postpone precipitation till just after the fuel is completely utilized. Also, for a given power we could choose voltage current values, which dynamically change, depending on concentration of fuel left. This would require an external circuit to regulate the require output if there is a constraint required on either current or voltage. Replacing NaOH with other additives, which do not share same ion as fuel/product and can help suppress hydrogen evolution when the solution is made, can also be a solution to improve the fuel cell run time.

6.2 Future work

On solubility model, we were able to improve it further by incorporating the change in temperature due to reactions and resistance losses. The model presented has been designed for 60°C and does not consider the dynamical temperature changes. In voltage-current model, temperature is one of the input parameter. There is a room to improve voltage current model based on statistical analysis of past results, presented in literature. There is a need to bring in temperature owing to the thermal energy released by the reactions and the losses.
Research also needs to be done on alternate alkali chemicals, which can help reduce immediate evolution of hydrogen gas when sodium borohydride solution is prepared. This might help increase the solubility limit of the solvents in absence of common ions.

Also research on technologies, which could help energy economical on cell separation like vacuum distillation, electro osmosis and anion exchange, can allow recirculation of water generated by the fuel cell. This is could considerably reduce the additional weight of water carried by the application source.
Bibliography


4. Scott Lux, Lifeng Gu, Grant Kopec, Robert Bernas, & George Miley, water management issues for direct borohydride / peroxide fuel cells, *fc-07-1201 (technical brief)*.

5. Chemical properties derived from webbook.nist.gov


## Appendix A: Energy sources

The following table presents the comparisons of specific energy of battery and fuel cells.

<table>
<thead>
<tr>
<th>Battery</th>
<th>Cell Type</th>
<th>Specific Energy (Whr/kg)</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lead–Acid</td>
<td>~40</td>
<td>Conventionally convenient</td>
<td>Very Low Specific Energy</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>High currents</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Low Specific Energy</td>
</tr>
<tr>
<td></td>
<td>Zinc–manganese</td>
<td>~80</td>
<td>Conventionally convenient</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Low Specific Energy</td>
</tr>
<tr>
<td></td>
<td>Zinc–manganese</td>
<td>~110</td>
<td>Conventionally convenient</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Higher performance</td>
<td>Low Specific Energy</td>
</tr>
<tr>
<td></td>
<td>Zinc–manganese (Alkaline)</td>
<td>~110</td>
<td>Conventionally convenient</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Higher performance</td>
<td>Low Specific Energy</td>
</tr>
<tr>
<td></td>
<td>Silver–Zinc</td>
<td>~110</td>
<td>Higher performance</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nickel–Cadmium</td>
<td>~60</td>
<td>Rechargeable</td>
<td>Very Low Specific Energy</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>High current</td>
<td>Self–discharging</td>
</tr>
<tr>
<td></td>
<td>Nickel–Metal hydride</td>
<td>~80</td>
<td>Rechargeable</td>
<td>Low Specific Energy</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Higher Specific Energy</td>
<td>Self–discharging</td>
</tr>
<tr>
<td>Fuel cell</td>
<td>Specific Energy (kJ/kg)</td>
<td>Performance</td>
<td>Fuel Logistics</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>-------------------------</td>
<td>-------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td>Lithium-ions</td>
<td>~150</td>
<td>Rechargeable</td>
<td>Flammable</td>
<td></td>
</tr>
<tr>
<td>Lithium primary</td>
<td>~200</td>
<td>Higher Specific Energy</td>
<td>Flammable</td>
<td></td>
</tr>
<tr>
<td>H₂ / Air</td>
<td>~340</td>
<td>High Performance</td>
<td>Not easy of Fuel Logistics</td>
<td></td>
</tr>
<tr>
<td>Methanol / Air</td>
<td>~400 – 1,000</td>
<td>High Performance</td>
<td>Fast Catalyst Degeneration</td>
<td></td>
</tr>
<tr>
<td>Borohydride / H₂O₂</td>
<td>400 – 1,000</td>
<td>Higher Performance</td>
<td>Higher Fuel Price</td>
<td></td>
</tr>
<tr>
<td>Borohydride / Air</td>
<td>450 – 2,000</td>
<td>High Specific Power &amp; Energy</td>
<td>Higher Fuel Price</td>
<td></td>
</tr>
</tbody>
</table>

Compared to batteries, fuel cell offer higher specific energy and thus higher run time for same quantity (weight) of fuel. And, it also offers flexibility to continuously supply fuel to generate power for theoretically unlimited time. Now, comparing among the fuel cells themselves, hydrogen oxygen fuel cells generate lower specific power and energy.
power and can be used for automotive and residential applications. For aerospace applications we need higher specific energy and methanol/air and sodium borohydride fuel cell can deliver the required output. Inflammability of methanol/air fuel cell might be of concern for the application. From this table, owing to high specific energy and its usability, sodium borohydride is an environmentally friendly and safe candidate for space and underwater applications.
Appendix B : Matlab Code

B.1 Solubility Model

File name: water with current

Used to: run the solubility module

NaBH4used=0;

NaBH4moles=fuel(t)/MwtNaBH4; %calculating no: moles of NaBH4

Namoles=NaBH4moles+NaOHmoles; %Calc Na moles constant through the reaction

BH4moles=NaBH4moles; %BH4 moles

charge=0; %do we need this?

NaBO2moles(t)=0;

perProduct(t)=0; %do we need this?

KSPNaBH4(t)=0;

KSPNaBO2(t)=0;

while and(and(KSPNaBH4(t)<154,H2O(t)>0),KSPNaBO2<16)

    t=t+1

    current(t)=current(t-1);

    N=current(t-1) * 60/f; %no: moles f electrons used in 1 minute

    NaBH4used=N/8; %8 moles of electrons consume 1 mole of NaBH4

    NaBH4moles(t)=NaBH4moles(t-1)-NaBH4used; %moles of Nabh4
BH4moles=NaBH4moles(t); %BH4 moles

H2O(t)=H2O(t-1)-N*2*MwtH2O/8-MwtH2O*N*lambda+waterin; % weight of water
KSPNaBH4(t)=Namoles*BH4moles/H2O(t)*1000; %Sol product defines as product
of no: moles per litre of water

NaBO2moles(t)=NaBO2moles(t-1) + N/8;

BO2moles=NaBO2moles(t);

KSPNaBO2(t)=Namoles*BO2moles/H2O(t)*1000;

voltageforwater

end

t=2:1:t;

KWH(t)=t*2.5/60;
B.2 Control file – to change initial conditions

File name: Control.m

Used for: Changing initial concentrations

clc; clear;

f = 96485.3399 ; % Faradays constant
MwtNaBH4= 37.8253 ; % M Wt NaBH4
MwtNaBO2 = 65.8 ; % M Wt NaBO4
MwtH2O = 18 ; % M Wt water
MwtNaOH = 40 ; % M Wt NaOH electron = 1.6022*10^-19; % Coulombs
AN = 6.023*10^23 ; % Avagadro number % note f = AN*electron
univ_r = 8.314 ; % Universal gas constant

% Variables

temp = 333.15 ; % temp

 t = 1; % Initializing time (Sec)
current(t) = 5 ; % Ampere Change
H2O = 500; % grams or ml

NaOH moles = 1/1000*H2O ; % (here 0.1 molar solution) 1 molar solutions is 1 mole per L
X = 30 ; % Initial conc of NaBH4 in %
fuel(t) = X/100*(H2O + NaOH moles*MwtNaOH)/(1-X/100);

% diffusion
lamda = 4.36;

H2O2 = 0.1;

waterin = 0.0 ; % ml/min so g/min
B.3 Voltage current model

File name : voltageforwater.m

% voltage drop calc

j = current(t-1)/25;  % current density (A/cm^2)

j_leak = 0.9;  % leakage current

ASR = .2005;  % (S^-1 cm^2)

jL = 2;  % limiting current density (A/cm^2)

etherm;

n_act = nAct(j,j_leak);

n_ohm = nOhmic(j, ASR);

n_conc = nConc(j,jL,j_leak);

V(t) = E_thermo-n_act-n_ohm-n_conc;

If V(t)<0.5
  break
end

V(1)=0.5;

vold=V(t-1);

vnew=V(t);

jnew=j*vold/vnew;

current(t)=jnew*25;

t;

power(t)=current(t)*vold;
File name: ethermo.m

Used for: Calculate theoretical voltage

\[ a = \text{NaBH}_4 \text{moles}(t); \]
\[ b = \text{NaBO}_2 \text{moles}(t); \]
\[ \text{univ}_r; \]
\[ \text{temp}; \]
\[ f; \]
\[ E_{\text{thermo}} = 2.24 - \left( \frac{\text{univ}_r \times \text{temp}}{8/f} \times \log \left( \frac{b}{a/H_2O_2^4} \right) \right); \]

File name: nconc.m

Used for: Calculating concentration loss

\textbf{function} out = nConc(jL_jL_jL_jL_jL)

\[ \text{alpha}_a = 0.45; \]
\[ c = \left( \frac{R \times T}{n \times F} \right) \times (1 + 1/\text{alpha}_a); \]

% Concentration losses

\[ \text{crt} = 57.9842; \% \text{correcting factor during normalization} \]
\[ \%jL = 2; \% \text{limiting current density (A/cm}^2) \]
\[ \text{out} = c \times \text{crt} \times \log(jL/(jL-(jL+jL_\text{leak}))); \]
File name: nact.m
Used for: Calculating activation loss

Function out = nAct(j, j_leak)

% Activation losses
alpha_a = .45;
alpha_c = .27,.4;
j_0a = .0001;
j_0c = .01;
n = 8; % num of electron transferred
corr=1;
k_a = (R*T/(alpha_a*n*F));
k_c = (R*T/(alpha_c*n*F));
anode = -k_a*log(j_0a)+ k_a.*log(j+j_leak);
cathode = -k_c*log(j_0c)+ k_c.*log(j+j_leak);
out = corr.*(anode + cathode);

File name: nOhmic.m
Used for: calculate Ohmic loss

function out = nOhmic(j, ASR)
crt=1;
out = j.*ASR*crt;
B.4 Code for plotting

File name : usetoplot.m

Used for : plot the results

figure(3)

plot(KWH(t),KSPNaBH4(t),'b--', KWH(t),154*ones(size(KWH(t))),'k-',
KWH(t),KSPNaBO2(t),'m:', KWH(t),16*ones(size(KWH(t))),'r-.');

legend('NaBH4','154','NaBO2','16');

xlabel('Time (W-Hr)','FontSize',14,'Interpreter','latex');

ylabel('Solubility product','FontSize',14,'Interpreter','latex');