Low voltage electrochemical hydrogen production

Eric P. Weaver

University of South Florida

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Low Voltage Electrochemical Hydrogen Production

by

Eric P. Weaver

A thesis submitted in partial fulfillment
of the requirements for the degree of
Department of Chemical Engineering
Master of Science in Chemical Engineering
College of Engineering
University of South Florida

Co-Major Professor: Burton Krakow, Ph.D.
Co-Major Professor: John Wolan, Ph.D.
Elias Stefanakos, Ph.D.

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DEDICATION

This work is dedicated to my wife, Sherida, and my daughters; Stefanie-Jo, Sharisse and Salisha, for their patience and support during the development of this research.

“Willing is not enough; we must do.”

Johann Wolfgang von Goethe
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LOW VOLTAGE ELECTROCHEMICAL HYDROGEN PRODUCTION

Eric P. Weaver

ABSTRACT

Hydrogen production is dependent on natural gas, 90% in the U.S. and 48% of the world’s production. Natural gas supply is dwindling and it’s price is increasing. Greenhouse gases and air pollutants are emitted when natural gas is used. In a single product production facility, coal is not competitive with natural gas for hydrogen production at current prices. Hydrogen production by direct electrochemical dissociation of water requires a relatively high voltage.

Techniques have been developed for manufacturing hydrogen as a lucrative byproduct of IGCC electric power generation, refinery sulfur production and sulfuric acid production for fertilizer production. Laboratory experiments have been conducted on small systems to advance the technology and full size commercial plants have been conceptualized and analyzed to establish economic viability.

In this thesis, a low voltage electrochemical hydrogen production technique has been developed that entails scavenging of the anode with sulfur dioxide. In an electrochemical cell hydrogen is produced at the negative electrode while the positive electrode is bathed in sulfur dioxide which is oxidized with water to sulfuric acid. The presence of SO₂ substantially reduces the equilibrium voltage relative to that required for the direct dissociation of water into hydrogen and oxygen. Also sulfuric acid is a more valuable byproduct than oxygen. More sulfuric acid is produced than any other chemical commodity in the U.S. and is a major economic indicator. Hydrogen produced by the electrochemical route being discussed in this thesis illustrates industrial possibilities for large scale-up, economical hydrogen production.
In an electrochemical cell, an equilibrium voltage of 1.23 volts is required to decompose water into hydrogen and oxygen. The presence of sulfur dioxide to scavenge the anode can reduce the equilibrium voltage from 1.23 volts to 0.17 volts. The equations shown below are reactions showing the energy requirements.

\[ 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 - 4 \text{ Faradays @ 1.2V} \]

\[ 2\text{SO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 + 2\text{H}_2 - 4 \text{ Faradays @ 0.17V} \]

The thermochemical free energy is reduced from 113kcal/mole to 15kcal/mole if sulfur dioxide is used as a scavenger.

In this work, extensive studies to determine the most effective electrodes and catalysts have been carried out. The possibilities for photo electrochemical implementation have been investigated and cell design optimization has been performed. Experimental methods and results will be presented and discussed.
CHAPTER 1

INTRODUCTION

1.1 Hydrogen Production Overview

The utmost importance to the evolution of the “Hydrogen Economy”, is a sustainable supply of hydrogen. Current methods of industrial scale hydrogen production are not sustainable. The primary source of industrial hydrogen is from steam reforming of natural gas also known as steam methane reforming (SMR). SMR accounts for approximately 48% of the world’s production of hydrogen and 90% of the United States’ production [1].

Oil reforming and coal gasification come in next at 30% and 18% respectively. Electrolysis ranks last in current industrial hydrogen production techniques at 4% [1]. Currently all of the above techniques involve CO$_2$ emissions thereby defeating the main purpose of the proposed switch to hydrogen. Even the electrolysis of water under current techniques involves CO$_2$ emissions because the electricity for electrolysis is provided by power plants where the electricity is predominantly produced from coal and natural gas.

The technical aspects of the preceding techniques, along with other techniques which are not yet performed at industrial scale will be briefly explained in the following sections. The advantages and disadvantages of the techniques will also be discussed.

1.1.1 Natural Gas Reforming

Natural gas reforming is also known as steam methane reforming due to its main constituent, methane. The first step in SMR is to pass methane and steam over a nickel catalyst at high temperature and pressure, $750^\circ$C -$1000^\circ$C and 15 atm – 25 atm respectively [2]. The resultant reaction is displayed in equation 1.

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2
\]  

(1)
The second step then oxidizes the CO using $\text{H}_2\text{O}$ as steam at 200°C-475°C, resulting in more hydrogen and $\text{CO}_2$ as equation 2 displays. This is known as the water-gas shift reaction.

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (2)$$

SMR is currently the most economical way to produce hydrogen and produces less $\text{CO}_2$ than other hydrocarbon based techniques. Yet, there are several issues against the use of SMR to fuel the “Hydrogen Economy”. The first issue is the production of $\text{CO}_2$. One of the key objectives in developing hydrogen as the main energy carrier is the reduction of greenhouse gases. With the development of $\text{CO}_2$ sequestration techniques this first issue could be corrected. However, this would probably affect SMR’s status as the most economical technique for producing hydrogen, because $\text{CO}_2$ sequestration adds considerable costs [3].

The next drawback is the instability of the cost of natural gas. The Cost of natural gas has a history of fluctuation and is projected to increase [4]. This situation would certainly be exacerbated by the increased demand introduced by large scale hydrogen production.

The final negative aspect of SMR as a long term hydrogen production technique is the supply of natural gas. There is much debate as to how long the world’s reserves of natural gas will last. The Energy Information Agency from the Department of Energy concludes that even counting on reserves that are not at present economically viable; the world possesses approximately 60 years worth of reserves at predicted consumption trends [4].

1.1.2 Oil Reforming

In oil reforming heavy hydrocarbons are first cracked or split into lighter hydrocarbons. They are then reformed similarly to natural gas. Hydrogen from oil produces even more $\text{CO}_2$ than natural gas. There is growing demand for oil and therefore prices are rising. There is political unrest in the Middle East where the greatest reserves of oil are located. Oil reserves are believed to be less than that of natural gas. The EIA estimates approximately 20 years worth of reserves at predicted consumption trends [4].
1.1.3 Coal Gasification

Experiments with coal gasification are documented as early as the 1600’s [5]. Several reactions occur to form syngas from coal. Reactions 3-6 below are the primary reactions for CO production.

\[
\begin{align*}
C + O_2 & \rightarrow CO_2 \quad (3) \\
C + CO_2 & \rightarrow 2CO \quad (4) \\
2C + O_2 & \rightarrow 2CO \quad (5)
\end{align*}
\]

Reaction 3 and 4 are exothermic. When temperatures are too great the solid waste ash, unreacted minerals from the coal, is possibly fused. To alleviate this problem, steam is added as shown in reaction 6.

\[
C + H_2O \rightarrow CO + H_2 \quad (6)
\]

The final step is the water-gas shift reaction as with steam methane reforming equation 2 [5].

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad (2)
\]

The temperatures and pressures for these reactions depend on the type of gasifier. Fixed bed gasifiers have a high temperature around 2100 °F and an exit gas temperature around 800 °F - 1200 °F. The operating pressure is 435 psig or greater. Fluidized bed gasifier has uniform temperature because it operates like a continuously stirred tank reactor (CSTR). Gas exits at the temperature of the reactions between 1700 °F and 1900 °F. Fluidized bed reactors operate between 5 and 435 psig. Entrained flow gasifiers also operate like a CSTR. They have an operating temperature between 2300 °F and 3200 °F. They have the highest operating pressure of the gasifiers at greater than 725 psig.

Coal gasification is considered by some, especially in the U.S, as the bridge to the “Hydrogen Economy” [6]. Reserves of coal are greater than other fossil fuels in the United States and throughout the world [4]. Additionally, coal’s cost is lower than other hydrocarbons [4].

Unfortunately coal has the largest carbon to hydrogen atomic ratio ranging from 2:1 to 1:1 compared to 1:2 for oil and 1:4 for methane. Coal reserves are larger than other fossil fuels but they are still not very plentiful.
At current usage rates the EIA estimates approximately 190 years of reserves, but with projected consumption rates, that drops to around 90 years of reserves [4].

1.1.4 Water Electrolysis

Water electrolysis closes out the list of current industrial hydrogen production techniques. Water is dissociated in an electrochemical reactor via an electrical bias across two electrodes in an aqueous alkaline solution. Electrons pass through the circuit created by a power source to the cathode. Hydrogen is created at the cathode. The reaction is represented by equation 7.

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \]  

(7)

The hydroxyl ions pass through the electrolyte to the anode forming oxygen, water and returning the electrons to the circuit. The resultant reaction is depicted in equation 8.

\[ 2\text{OH}^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \]  

(8)

The overall reaction is equation 9.

\[ \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2 \]  

(9)

The theoretical voltage needed for this reaction is 1.23 volts. The applied voltage will be higher than the theoretical voltage, typically 1.65-1.8 volts [7], due to overvoltage, an effect caused by system resistance, reaction kinetics at the electrode surfaces and concentration gradients.

Currently, water electrolysis is the most expensive industrial hydrogen production technique[7]. This will change in the near future because the cost of fuels is projected to go up and the capitol cost of electrolyzers is projected to go down [8] [9] [10]. Water electrolysis itself produces no harmful byproducts or waste. The only products are hydrogen and oxygen. The problem with electrolysis lies in the amount of power needed and the source of the electric power. The voltage is too high for single band gap and thin film semiconductors which produce between 0.5 and 0.7 volts. These are the most common solar cells used currently for photovoltaic cells.

In order to use these cells they must be connected in series to obtain the required voltage. This means it takes 3 to 4 cells to meet the voltage requirements. Therefore, these cells can not be placed directly in the electrolyte and used as the electrodes.
Both of these facts cause an increase in cost and a loss of efficiency because the single crystal silicon solar cells producing 0.5 volts are the most efficient solar cells made commercially.

If electricity from power plants is used, carbon dioxide is still released because hydrocarbons are currently used as fuel in the majority of power plants. If CO₂ sequestration is implemented, benefits are increased because sequestration is much easier and cost effective at point-sources like power plants. Most people envision mass hydrogen production with electrolysis and alternative energy sources like wind and solar. With the current pricing structure, alternative sources can not compete economically. Some people propose nuclear as the power source of choice. Even if the environmental arguments are addressed, the political aspects of nuclear power leave its future questionable.

1.1.5 Alternative Hydrogen Sources

Research on using biomass and waste to produce hydrogen is at this time a highly active area. Biomass includes crops grown specifically as fuel stock, waste from agricultural crops, wood chips and many other organic wastes. Researchers are looking into sugar cane waste, orange peel waste, fast growing trees and grasses along with other sources of biomass in Florida. Biomass and solid waste can be gasified similar to coal or added to coal. Unfortunately it is far less efficient. Research to improve the conversion of biomass to syngas and production of hydrogen from syngas is being done and can make this a more viable option [11].

Work is being done with multijunction semiconductors to increase the voltage output in a photoelectrochemical cell. These cells can be more expensive to make and are less efficient than single junction solar cells. The U.S. National Renewable Energy Laboratory (NREL) has improved on these efficiencies using a combination of photovoltaic and photoelectrochemical cells [11].

Biological techniques are being studied that adapt photosynthesis for hydrogen production which include biophotolysis of water by microalgae and cyanobacteria.
Other biological techniques study bacteria that decompose organic compounds, such as sugar or starch bearing waste waters, and produce hydrogen. So far costs are high and efficiencies are low.

1.2 Scope of this Thesis

The first intent of this work is to determine if two of the hydrogen production techniques of interest to this group are economically viable. The technical and historical importance of these two techniques will be discussed with the economic analysis. The two techniques that economical analyses are done on are electrochemical dissociation of \( \text{H}_2\text{S} \) to hydrogen and sulfur and the electrochemical oxidation of \( \text{SO}_2 \) with \( \text{H}_2\text{O} \) to produce hydrogen and sulfuric acid.

Next, improvements on an existing electrolysis cell for \( \text{SO}_2 \) oxidation to inhibit the flow of sulfur dioxide to the cathode compartment are evaluated. Previous work done with this cell suggested the use of tungsten carbide as a catalyst [12]. Tests with tungsten carbide electrodes will be discussed. Redesign of the control and data acquisition systems for this cell and later cells will be presented.

An electrolysis cell redesign to implement smaller electrodes to facilitate the use of catalyst deposition techniques available to the group will be described. These catalyst deposition techniques and results from experiments with these catalysts will be discussed. The conversion of this cell design to a cell utilizing a polymer electrolyte for experiments similar to historical work [13] will be presented.

Conclusions developed from experimental results will be drawn out and suggestions for further work will be presented. Some of the technical aspects of the future work will be discussed.
2.1 Overview

Vast amounts of hydrogen will be needed to fuel the “Hydrogen Economy”. Two of the techniques researched by our group can be utilized in conjunction with the production of sulfuric acid which has higher production than any chemical commodity in the United States. This could constitute more hydrogen than is currently produced by all techniques.

Sulfuric acid is manufactured by oxidizing sulfur dioxide with oxygen from air. If the oxygen were derived from water by the electrochemical route being developed in this project, large quantities of hydrogen would be produced as a valuable byproduct. Table 2.1 demonstrates how much hydrogen can be produced as a result of commercialization of this and other byproduct reactions of sulfur compounds that our group is studying. It shows that these processes can produce almost 3 times the current annual production of H₂ in the United States within current sulfuric acid production levels. Our attention currently stresses the oxidations of SO₂ and H₂S, which by themselves can produce 1/3 more hydrogen than is produced now.

**Table 2.1 Hydrogen Production**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Hydrogen Yield (10⁹ kg)</th>
<th>Free Energy (Kcal/mol)</th>
<th>Equilibrium Voltage (V)</th>
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<tr>
<td>H₂S → S+H₂ @ 400K</td>
<td>0.8</td>
<td>9</td>
<td>0.19</td>
</tr>
<tr>
<td>2H₂O+S → SO₂+2H₂</td>
<td>1.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2H₂O+SO₂ → H₂SO₄+H₂</td>
<td>0.8</td>
<td>15</td>
<td>0.17</td>
</tr>
<tr>
<td>Total</td>
<td>3.2</td>
<td>-</td>
<td>-</td>
</tr>
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</table>

Merchant Hydrogen Production in 2000 = 1.2 X 10⁹ Kg
2.2 Electrochemical Hydrogen Sulfide Dissociation

The economic analysis of hydrogen sulfide dissociation was performed to compare our electrochemical process to the typical Claus Process in IGCC power plants and refineries. Both analyses provide legitimate reason for further investigation into this process.

2.2.1 IGCC Power Plants

The FutureGen program that President Bush supports is based on integrated gasification combined-cycle technology (IGCC). Figure 2.1 illustrates a FutureGen power plant.

In an IGCC's gasifier, carbon-based raw material reacts with steam and oxygen at high temperature and pressure to produce combustible synthesis gas. The gasifier's high temperature vitrifies inorganic materials into a course, sand like material, or slag that is sold for road building. The synthetic fuel leaves the gasifier and is further cleaned of impurities. It is used in the system to run primary and secondary gas and steam turbines, similar to a natural gas combined-cycle generating system.

Figure 2.1 FutureGen Power Plant Schematic
The primary environmental benefits include increased efficiency and nearly zero air pollution. Most pollutants are removed before combustion and are not created when the fuel is burned. In the case of sulfur, it is collected in a form that can be sold. This is a big change for conventional coal plants, where even clean ones produce a lake-sized impoundment of sulfuric slurry by pulling sulfur compounds from the stack flue gas. IGCC power plants are the cleanest coal-based power generation facilities in the world.

The capital cost for an IGCC power plant is greater than for a conventional plant. This is partly justified by higher efficiency, lower emissions and the potential for producing byproducts. However, the bottom line is that conventional coal and natural gas fired power plants can produce electric power at a lower net cost. While increased fuel costs and environmental regulations may eventually close this gap, technical improvements are needed to help achieve this and remove the economic barrier to deployment of these cleaner and more efficient systems.

2.2.1.1 Sulfur Removal

IGCC power plants now in operation extract the sulfur from the synthesis gas as hydrogen sulfide. The hydrogen sulfide is extracted along with carbon dioxide in a stream called acid gas. Partial oxidation of the acid gas with air yields elemental sulfur and water (Claus Process) with a waste stream of dilute carbon dioxide in nitrogen. The process is illustrated in figure 2.2. There is one IGCC plant that uses complete oxidation of hydrogen sulfide to sulfuric acid. The sulfur recovery systems of IGCC power plants can be improved and thereby produce an additional revenue stream that will lower the cost of IGCC electricity.

2.2.1.2 Proposed Process

Electrolytic oxidation of the extracted hydrogen sulfide can yield sulfur and hydrogen. The carbon dioxide is separated before electrolysis which leaves a concentrated carbon dioxide waste stream which is easier to sequester. This process is illustrated in Fig. 2.2. The value of the hydrogen makes the system more profitable.
The energy benefit of electrolytic decomposition of the H\textsubscript{2}S as compared to decomposing water is illustrated in Equations (10) and (11).

\begin{align*}
\text{H}_2\text{S}(g) &\rightarrow \text{S}(l) + \text{H}_2(g) - 2 \text{ Faradays } @ 0.19\text{V} \quad \Delta G^\circ = 8.9 \text{ kcal/mole } @ 400\text{K} \quad (10) \\
\text{H}_2\text{O}(l) &\rightarrow \text{H}_2(g) + \text{O}_2(g) - 2 \text{ Faradays } @ 1.2\text{V} \quad \Delta G^\circ = 57 \text{ kcal/mole} \quad (11)
\end{align*}

### 2.2.1.3 Economics

The scale of the plant developed for this techno-economic analysis is for replacement of the sulfuric acid production plant at TECO’s Polk Power Station IGCC power plant in Florida. It is a nominal 250 MW (net) IGCC power plant. This is a comparable size to the Wabash River IGCC power plant which has a nominal 262 MW (net) rating. The plant design includes separation of the acid gas into its two main constituents, CO\textsubscript{2} and H\textsubscript{2}S.

The separation of CO\textsubscript{2} and H\textsubscript{2}S minimizes the flow through the electrolyzer and facilitates CO\textsubscript{2} sequestration. A waste stream from the electrolyzer is separated into its components for recycling or disposal.
The economics of this process rely heavily on power costs and electrolyzer pricing. When dealing with electrolysis, cost optimization of these two parameters is needed. There is currently not enough technical information on current density and voltage requirements to perform this optimization. A reasonable current density of 2000 A/m$^2$ at 0.7 volts is used. It is assumed that similar costs as those published in literature for water electrolyzers will apply. Literature values for electrolyzers currently range from $2280/m^2$-$2850/ m^2$. Costs are projected to drop to $356/ m^2$-$855/ m^2$ as technological advances are made [8] [9] [10]. Table 2.2 shows the economics calculated at the short term cost of $2280/m^2$.

**Table 2.2 IGCC Economic Analysis**

<table>
<thead>
<tr>
<th>POWER PLANT PARAMETERS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>IGCC Plant Capacity (Gross MW)</td>
<td>315</td>
</tr>
<tr>
<td>Sulfur Production (Tons/day)</td>
<td>63</td>
</tr>
<tr>
<td>Coal sulfur content (%)</td>
<td>2.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ELECTROLYSIS PLANT INVESTMENTS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparatus to Remove Carbon Dioxide</td>
<td>$586,849</td>
</tr>
<tr>
<td>Electrolyzer</td>
<td>$4,560,000</td>
</tr>
<tr>
<td>Balance of Plant</td>
<td>$6,213,151</td>
</tr>
<tr>
<td>Total Electrolysis Plant Investments</td>
<td>$11,360,000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ANNUAL CAPITAL AND O&amp;M COSTS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Annualized Capital Costs</td>
<td>$1,730,000</td>
</tr>
<tr>
<td>Labor</td>
<td>$516,000</td>
</tr>
<tr>
<td>Catalysts, water and other operating costs</td>
<td>$632,417</td>
</tr>
<tr>
<td>Electricity</td>
<td>$2,500,000</td>
</tr>
<tr>
<td>Total Annual Capital and O&amp;M Costs</td>
<td>$5,378,417</td>
</tr>
</tbody>
</table>
Table 2.2 Continued

<table>
<thead>
<tr>
<th>HYDROGEN PRODUCTION COSTS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Costs to Produce 1 Ton of S + 125 lb. of H₂</td>
<td>$245</td>
</tr>
<tr>
<td>Avoided Cost of Claus Process/Ton of S</td>
<td>$137</td>
</tr>
<tr>
<td>Net Production Cost of 125 lb. of H₂</td>
<td>$108</td>
</tr>
<tr>
<td>Net Production Cost of 1 lb. of H₂ Gas</td>
<td>$0.86</td>
</tr>
<tr>
<td>Hydrogen Liquefaction Cost ($/lb.)</td>
<td>$0.55</td>
</tr>
<tr>
<td>Net Production Cost of 1 lb. of Liquid H₂</td>
<td>$1.41</td>
</tr>
<tr>
<td>MARKET PRICE OF LIQUID H₂ ($/LB.)</td>
<td>$2.00</td>
</tr>
<tr>
<td>GROSS PROFIT ON LIQUID H₂ ($/LB.)</td>
<td>$0.59</td>
</tr>
<tr>
<td>Savings to Electrical Production Cost ($/MWh)</td>
<td>$0.63</td>
</tr>
</tbody>
</table>

2.2.1.4 Carbon Dioxide Sequestration Economics

The electrolytic production of hydrogen and sulfur never generates any carbon dioxide. However, there is carbon dioxide in the hydrogen sulfide feedstock extracted from the synthesis gas. Processing the feedstock for byproduct hydrogen production can facilitate sequestering of this carbon dioxide at a cost far lower than conventional flue gas separation and sequestering. The proposed separation process costs approximately $21/ton C. The DOE website on CO₂ sequestration estimates carbon storage, transportation, and sequestration to cost approximately $50/ton C [3]. The economics of CO₂ sequestration are laid out in Table 2.3. The CO₂ capture cost of $21/ton C is not listed in Table 2.3 as a cost because it is already accounted for in the cost of H₂ production.

When the acid gas of an IGCC power plant is partially oxidized with air in the Claus process, the rejected CO₂ is mixed with a large quantity of nitrogen. For sequestering, the carbon dioxide has to be separated from the nitrogen or sequestered together with the nitrogen. These are both undesirable. The DOE website on CO₂ sequestration estimates carbon capture in dilute streams to cost approximately $150/ton C [3]. If carbon emission reductions are mandated as they are in Europe, CO₂ trading prices will likely follow prices in Europe.
The price for CO$_2$ credits on the European Climate Exchange as of 27 Jun, 2005 is $38.01/ ton CO$_2$[14]. This is the value for captured CO$_2$ used in Table 2.3. The table clearly shows that sequestration of the concentrated CO$_2$ captured in the proposed process is economically beneficial at the European trading price for CO$_2$. It also shows that capture and sequestration of the diluted CO$_2$ from the current process would lose money at the European trading price for CO$_2$.

**Table 2.3 CO$_2$ Sequestration Economics**

<table>
<thead>
<tr>
<th>Projected Carbon Sequestration Economics</th>
<th>Proposed Process</th>
<th>Current Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGCC Plant Capacity (Gross MW)</td>
<td>315</td>
<td>315</td>
</tr>
<tr>
<td>Acid Gas Stream Carbon (tons/hr)</td>
<td>3.04</td>
<td>3.04</td>
</tr>
<tr>
<td>Carbon Costs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Capture Cost ($/ton C)</td>
<td>0</td>
<td>150</td>
</tr>
<tr>
<td>Additional Cost for Storage,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transportation and Sequestration ($/ton C)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Carbon Value</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$ Trading Price ($/ton CO$_2$)</td>
<td>38.01</td>
<td>38.01</td>
</tr>
<tr>
<td>CO$_2$ Trading Price ($/ton C)</td>
<td>139.38</td>
<td>139.38</td>
</tr>
<tr>
<td>Profits or Losses</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Profits From Collection, Storage,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transportation and Sequestration ($/ton C)</td>
<td>89.38</td>
<td>-60.62</td>
</tr>
<tr>
<td>Profits From Collection, Storage,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transportation and Sequestration ($/MWh)</td>
<td>0.86</td>
<td>-0.58</td>
</tr>
</tbody>
</table>

The cost for IGCC power is greater than for conventional electric power. Rule of thumb estimates say the difference is around $10-$20/MWh. Tables 2.2 and 2.3 show the proposed process can help reduce that cost difference. The initial profits from H$_2$ sales reduce that difference by $0.63/MWh. Long term projections for H$_2$ profits will reduce that difference by $1.38/MWh.
If carbon emission reductions are mandated, as they are in Europe, sequestration of the concentrated CO₂ captured in the proposed process would provide an additional economic benefit of $0.86/MWh. This gives a near term savings of $1.49.

2.2.1.5 Technical Approach

Hydrogen sulfide will be decomposed at a temperature at which sulfur is a low viscosity liquid so that it can run out of the electrolytic cell quickly and easily. The solid line curve in figure 2.3 gives the viscosity of liquid sulfur and shows that it is minimized near 150°C. We will operate near this temperature.

To do this we are seeking to exploit some recent developments in solid state electrolytes. These involve inorganic crystals whose proton conductivities rise rapidly with temperature. One of these is cesium hydrogen sulfate whose conductivity is shown by the dashed curve in Figure 2.3. The conductivity scale is logarithmic. The conductivity goes up by about 5 orders of magnitude between 120 and 150°C and the material is a good conductor at the temperature where we want to work.

Figure 2.3 Viscosity of Sulfur, Conductivity of CsHSO₄ vs Temperature
2.2.2 Refineries

Refineries create and use hydrogen using SMR. They also have a hydrogen sulfide waste stream that needs treatment. They currently use the Claus process similar to IGCC power plants. The electrochemical split of hydrogen sulfide can produce hydrogen for some of the needs thereby reducing CO\textsubscript{2} emissions from SMR.

A graphical comparison of the two processes is depicted in figure 2.4. An economic analysis was performed to compare the existing technology to the electrochemical approach.

![Diagram of Claus Process and Electrolysis](image)

**Figure 2.4 Refineries with Claus Process and Electrolytic Process**

2.2.2.1 Economics

The same sulfur capacity plant of 63 tons per day was evaluated for the refinery analysis. The plant is considerably smaller due to a cleaner hydrogen sulfide stream. Additional separation equipment is not needed to purify the hydrogen sulfide before the electrolyzer. This lowers the capitol cost of the plant for refineries as compared to IGCC power plants. The same assumptions about electrolyzer costs were made.

The costs used for the analysis are displayed in table 2.4. The comparison of costs for the two processes and the determined savings are in table 2.5.
### Table 2.4 Refinery Electrolysis Plant Costs

<table>
<thead>
<tr>
<th>ELECTROLYSIS PLANT INVESTMENTS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyzer</td>
<td>$4,560,000</td>
</tr>
<tr>
<td>Balance of Plant</td>
<td>$3,428,365</td>
</tr>
<tr>
<td><strong>Total Electrolysis Plant Investments</strong></td>
<td><strong>$7,988,365</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ANNUAL CAPITAL AND O&amp;M COSTS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Annualized Capital Costs</td>
<td>$1,216,680</td>
</tr>
<tr>
<td>Labor</td>
<td>$336,195</td>
</tr>
<tr>
<td>Catalysts, water and other operating costs</td>
<td>$625,149</td>
</tr>
<tr>
<td>Electricity</td>
<td>$1,821,315</td>
</tr>
<tr>
<td><strong>Total Annual Capital and O&amp;M Costs</strong></td>
<td><strong>$3,999,339</strong></td>
</tr>
</tbody>
</table>

### Table 2.5 Refinery Sulfur Processing Comparison

<table>
<thead>
<tr>
<th>Typical Refinery Costs/Day–Current</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Costs to Produce 63 Ton of S @$137/T</td>
<td>$8,631</td>
</tr>
<tr>
<td>Hydrogen Cost (7875# @$0.60)</td>
<td>$4,725</td>
</tr>
<tr>
<td><strong>Total Cost/Day</strong></td>
<td><strong>$13,356</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrochemical Hydrogen Production$/Day</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen &amp; Sulfur Production Cost</td>
<td>$11,938</td>
</tr>
<tr>
<td>Daily Electrochemical Savings</td>
<td>$1,418</td>
</tr>
<tr>
<td><strong>Potential Yearly Saving (335days/year)</strong></td>
<td><strong>$475,030</strong></td>
</tr>
</tbody>
</table>

The preceding table shows the process looks attractive. Additional savings could be made in the event of carbon taxes due to reduced CO₂ emissions.
2.3 Electrochemical Hydrogen and Sulfuric Acid Production

The economic analysis of hydrogen and sulfuric acid production was performed to compare our electrochemical process to a typical sulfuric acid production plant in the manufacture of fertilizers. The analysis provides legitimate reason for further investigation of this process.

2.3.1 Sulfuric Acid Production

As stated in the introduction to this chapter sulfuric acid is typically produced by first oxidizing sulfur to sulfur dioxide. Air is initially passed through a dryer to eliminate moister that could condense and corrode equipment further down the line. The dryer is an absorption tower with sulfuric acid which is very hygroscopic and therefore easily absorbs the water in the air. The air is then compressed to a level high enough to provide a pressure difference through the entire plant. Excess air is then fed to a burner with sulfur that produces sulfur dioxide and heat. The reaction in the burner is given by equation 12.

\[ S + O_2 \rightarrow SO_2 + \text{Heat} \quad (12) \]

The sulfur dioxide is then passed into a catalytic converter over a catalyst. The sulfur dioxide is oxidized by the some of the excess air to produce sulfur trioxide and more heat. This oxidation reaction is shown in equation 13.

\[ SO_2 + \frac{1}{2} O_2 \rightarrow SO_3 + \text{Heat} \quad (13) \]

These gases now consist of air, sulfur dioxide and sulfur trioxide. They are passed through what is typically called an interpass absorber where sulfur trioxide is removed and the sulfur dioxide and air are returned to the catalytic converter. This shifts the equilibrium of the sulfur dioxide oxidation reaction and improves the conversion.

The final product from the catalytic converter and the sulfur trioxide from the interpass absorber are passed through the final absorber with water. This produces between 93% to 98% sulfuric acid by weight. The reaction from this mixture is expressed in equation 14.

\[ SO_3 + H_2O \rightarrow H_2SO_4 + \text{Heat} \quad (14) \]
As can be seen by equations 12, 13 and 14, the current process for sulfuric acid manufacture produces a lot of heat. As stated earlier, this heat is used to make electricity. This amount of heat produces more energy than the sulfuric acid plant consumes. The electricity can be used in the balance of the fertilizer plant or sold to the local utility. This is denoted as a negative energy cost in the economic analysis.

### 2.3.2 Proposed Process

A low voltage electrochemical hydrogen production technique has been developed involving scavenging of the anode with sulfur dioxide. In an electrochemical cell with a sulfuric acid electrolyte hydrogen is produced at the negative electrode while the positive electrode is bathed in sulfur dioxide which is oxidized to sulfuric acid. The presence of SO$_2$ to scavenge the anode substantially reduces the equilibrium voltage relative to that required for the direct dissociation of water into hydrogen and oxygen as can be seen in equations 15 and 16.

\[
\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2 \quad @ 0.17 \text{ V} \Delta G_0 = 15 \text{ kcal/mol} \quad (15)
\]

\[
2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 \quad @ 1.2 \text{ V} \Delta G_0 = 113 \text{ kcal/mol} \quad (16)
\]

Sulfuric acid is a more valuable byproduct than oxygen. The differences between a typical sulfuric acid plant and the proposed electrochemical plant are shown in figure 2.5.

Figure 2.5 Comparison of Current Acid Process and Electrochemical Alternative
2.3.3 Plant Design and Economic Analysis

The concept plant for the economic analysis is based on a replacement plant for current 3500 tpd H\textsubscript{2}SO\textsubscript{4} plant. It is assumed that the sulfur burner, heat exchangers, piping, etc. are unchanged on a cost basis. The plant concepts were designed and priced by Chemcad modeling, discussion with industry, and plant design estimations [15].

The SO\textsubscript{2}/N\textsubscript{2} separation unit was modeled in Chemcad and priced using plant design estimates [15]. A combination of compression, cooling and absorption were used in the model for SO\textsubscript{2}/N\textsubscript{2} separation.

The sulfuric acid concentration unit was modeled in Chemcad and priced as the SO\textsubscript{2}/N\textsubscript{2} separation unit. The concept for the sulfuric acid concentration unit is for vacuum distillation. The pricing compared very closely to the vacuum flash system by Aker Kvaerner Chemetics. Discussions with Aker Kvaerner Chemetics were the starting point for design parameters of the distillation system.

The economics of this process rely heavily on power costs and electrolyzer pricing. When dealing with electrolysis, cost optimization of these two parameters is needed. There is currently not enough technical information on current density and voltage requirements to perform this optimization. A current density of 2000 A/m\textsuperscript{2} at 0.7 volts is used. This current density is reported in literature. It is assumed that similar costs as those published in literature for water electrolyzers will apply. Literature values for electrolyzers currently range from $2280/m\textsuperscript{2}$-$2850/m\textsuperscript{2}$. Costs are projected to drop to $356/m\textsuperscript{2}$-$855/m\textsuperscript{2}$ as technological advances are made [8] [9] and [10]. Table 2.6 shows the economics calculated at the short term cost of $2280/m\textsuperscript{2}$.

**Table 2.6 Sulfuric Acid Plant Economic Comparison**

<table>
<thead>
<tr>
<th>Economic Evaluation Assumptions (SO\textsubscript{2} Electrolysis)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Production (tons/day 98% H\textsubscript{2}SO\textsubscript{4})</td>
<td>3500</td>
</tr>
<tr>
<td>Production (tons/day H\textsubscript{2})</td>
<td>71.4</td>
</tr>
<tr>
<td>Plant Operation Life (yrs)</td>
<td>30</td>
</tr>
<tr>
<td>Electrical Energy Cost (2002 $/MWh)</td>
<td>40</td>
</tr>
<tr>
<td>Cost of Capital (%)</td>
<td>15</td>
</tr>
</tbody>
</table>
Table 2.6 Continued

<table>
<thead>
<tr>
<th>Economic Evaluation</th>
<th>Current Process</th>
<th>Electrochemical Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Capital (MM$)</td>
<td>51.2</td>
<td>133.8</td>
</tr>
<tr>
<td>Annualized Cost(MM$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital</td>
<td>7.8</td>
<td>20.4</td>
</tr>
<tr>
<td>O &amp; M</td>
<td>32.6</td>
<td>42.1</td>
</tr>
<tr>
<td>Utilities</td>
<td>-7.5</td>
<td>21.1</td>
</tr>
<tr>
<td>Total cost of Products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>($/ton H$_2$SO$_4$)</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>($/ton H$_2$SO$_4$ + 40 lb H$_2$)</td>
<td>66.44</td>
<td></td>
</tr>
<tr>
<td>Cost Difference</td>
<td>42.44</td>
<td></td>
</tr>
<tr>
<td>gH$_2$ Cost($/lb H$_2$)</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>LH$_2$ Cost ($/lb H$_2$)</td>
<td>1.68</td>
<td></td>
</tr>
</tbody>
</table>

2.3.4 History

In the 1970’s and early 1980’s Westinghouse in the U.S. and the European Commissions Joint Research Centre (JRC) in Ispra, Italy investigated what became known as the Westinghouse cycle or Mark 11. The sulfur cycle is so called because like the main focus of this thesis sulfur dioxide is used to depolarize the anode in an electrolyzer to form hydrogen and sulfuric acid, but unlike this thesis the sulfuric is decomposed to water, oxygen and sulfur dioxide so the sulfur dioxide can be recycled. The sulfur cycle is represented by equations 17, 18 and 19.

\[
\begin{align*}
SO_2 + 2H_2O & \rightarrow H_2SO_4 + H_2 & (17) \\
H_2SO_4 & \rightarrow SO_3 + H_2O & (18) \\
SO_3 & \rightarrow SO_2 + \frac{1}{2} O_2 & (19)
\end{align*}
\]

Equations eighteen and nineteen are very energy intensive. Equation eighteen requires temperatures of around 700 K. Nineteen requires a temperature of 1200 K [16].
The economic analysis for this thesis did not consider the requirements for equations 18 and 19 because at current and near term production needs for hydrogen it is more economical to sell the sulfuric acid. In the future it may be necessary to decompose the acid if this technique is used to produce more hydrogen and therefore more sulfuric acid than the market can handle. At that time it would be essential for solar heat collection or possibly nuclear waste heat to be used for the heat requirements of sulfuric acid decomposition in order to maintain favorable economics with such high energy requirements. Westinghouse discussed both of the possibilities for thermal inputs [17] [18]. The energy requirements for the Westinghouse process were estimated in an article by D. Van Velzen and placed in the table 2.7 [16].

<table>
<thead>
<tr>
<th></th>
<th>65% H_2SO_4</th>
<th>55% H_2SO_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity (0.62V)</td>
<td>315 KJ/mol</td>
<td>315 KJ/mol</td>
</tr>
<tr>
<td>Concentration Step</td>
<td>169 KJ/mol</td>
<td>240 KJ/mol</td>
</tr>
<tr>
<td>Thermal Dissociation</td>
<td>272 KJ/mol</td>
<td>272 KJ/mol</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>756 KJ/mol</strong></td>
<td><strong>827 KJ/mol</strong></td>
</tr>
</tbody>
</table>

Investigations in Germany determined what might be acceptable parameters for an electrolytic cell. They developed a 3 compartment cell that had a center compartment with flowing 30% H_2SO_4 between two cation exchange membranes. They used graphite felt for the electrodes. The cathode felt was platinized. They used a homogeneous catalyst HI in the anode compartment. The German group also did work with optimizing the carburization of WO to form WC electrodes which they determined looked promising as catalytically active cathodes [19].

Westinghouse reported results better than those used for the economics of this thesis. They reported achieving 200 mA/cm^2 at only 0.6 V. They used a bipolar membrane electrolyzer with carbon porous flow through electrodes. They reported using ruthenium oxide as the catalyst on both anode and cathode.
2.3.5 Technical Approach

There are two different technical approaches for the electrolyzer considered in this thesis. The first studied involved only a liquid electrolyte, sulfuric acid. The first cell was designed strictly for this purpose. It can be seen in figure 2.6. This design easily facilitates the switch to a low band gap single junction solar cell when the voltage requirements are met by the optimized design parameters. This design requires a flow gradient to restrict flow of sulfur dioxide from the anode compartment to the cathode compartment. This cell was operated at ambient temperature and 100 psi. The design parameters are discussed in an earlier thesis [12].

![Figure 2.6 Four-Inch Diameter Electrode Cell](image)

It was determined that smaller electrodes might facilitate catalyst deposition better than the four inch electrodes for the group. A cell to utilize two inch diameter or two inch square electrodes was developed. This second design was easily manipulated for use with liquid electrolyte as the first design, solid electrolyte, or a combination of both. It was designed for use of materials readily available locally and materials that could be adapted without use of the machine shop. Diagrams of the cells for two inch electrodes will be shown in the experimental results section. These cells were operated at ambient temperature and 0-90 psig.
CHAPTER 3

FOUR-INCH DIAMETER ELECTRODE CELL

3.1 Overview

The first work done towards this thesis was a continuation of the work done by Chettiar [12]. This work was done with the four inch diameter cell briefly described at the end of the last chapter. It had been proven with the four inch cell that process was producing relatively pure hydrogen at potentials lower than water electrolysis. It appeared the use of tungsten carbide lowered the overpotential but the adhesion of the evaporated tungsten carbide was not sufficient.

3.2 Design Issues

Where the previous work had let off there were still some design issues with the four inch cell. First the diffusion of sulfur dioxide to the cathode was significantly slowed down but was never stopped. Another issue is the fact there was still considerable overpotential adherent with the four inch cell. The previous thesis by Chettiar concluded that tungsten carbide and ruthenium oxide as catalysts could reduce some of this overpotential [12].

Finally the window for the four inch cell was susceptible to cracking and therefore a Teflon and aluminum replacement had to be installed. The lack of a window requires a system for sensing the hydrogen pocket in the cell as described by Chettiar [12]. This adds to the complexity of the overall system and the lack of a window means design changes will be needed to facilitate the use of a solar cell to replace the electrodes.
3.3 Design Changes

The first design change was a remodel of the stand for the four inch cell. It had been determined that the most probable reason for the glass window breakage was the added stress to two of the bolts for sealing the system caused by use of those same two bolts for attachment of the cell to the stand, see figure 2.6.

The stand was redesigned with a ring that the entire base of the cell could sit on therefore creating no stress points in the cell. See figures 3.1 and 3.2. A window rated at 500 psi instead of 200 psi was also purchased for added assurance.

Figure 3.1 New Four-Inch Electrode Cell Base

Figure 3.2 Four-Inch Electrode Cell and New Base
The next two design changes were implemented to deter sulfur diffusion to the cathode compartment. It was noted that sulfur build up on the cathode due to sulfur dioxide diffusion started at the bottom of the cathode. It was postulated that possibly a flow gradient was created by hydrogen bubble evolution and introduction of sulfuric acid to the cathode compartment through a tube facing up the cathode, see figure 2.6 item 17. This flow gradient could possibly have been pulling fluid from the bottom of the cell and/or forcing sulfuric acid over the top of the cathode to the anode compartment then out the exit at the bottom of the anode compartment. This flow of acid from the cathode to the anode compartment could force the sulfuric acid and sulfur dioxide from the center of the anode to the bottom then through the electrolyte bridge to the cathode compartment. Another possibility determined was that due to the fact that liquid sulfur dioxide is denser than 20% sulfuric acid, the sulfur dioxide introduced at the center of the anode could be sinking to the bottom of the anode compartment. This would leave a short path across the electrolyte bridge to the cathode compartment.

The first design change to stop sulfur dioxide diffusion due to the previously stated reasons was to extend the insulator between the two electrodes to the bottom of the cell and seal off that section of the electrolyte bridge, see figure 2.6 item 16. The second change to slow sulfur dioxide diffusion was to place a 180 degree bend in the end of the cathode sulfuric acid inlet to deter an upward flow gradient of sulfuric acid, see figure 3.3.

Figure 3.3 Four-Inch Electrode Cell with New H₂SO₄ Inlet Tube
The last change implemented to the four inch cell was due to previous misfortune with catalyst deposition. Instead of depositing tungsten carbide as a catalyst, tungsten carbide electrodes were purchased.

3.4 Flow System

The same flow system as described by Chettiar [10] was used in the operation of the four inch cell. The flow diagram as depicted by Chettiar [10] is seen in figure 3.4. Liquid sulfur dioxide and dilute sulfuric acid are pumped into the bottom center of the cell using two separate piston metering pumps.

Figure 3.4 Four-Inch Diameter Electrode Cell Flow Diagram

A third metering pumps creates a flow gradient from the cathode compartment to the anode compartment by pumping dilute sulfuric acid into the cathode compartment at a greater rate than it is pumped into the anode compartment.

Pressure in the cell is controlled by a 100 psi back pressure regulator in the product acid line at the bottom of the cell. Pressure is monitored by a teflon pressure transducer monitored by a Labview program.
Hydrogen is released from the cell through a micrometering valve and bubbled through water into a gas collection cylinder. Gas samples can be taken before or after bubbling through water through a septum or collected in an infrared cell.

3.5 Control System

The control system discussed by Chettiar for earlier work with the four inch cell was not implemented for the experiments with the four inch cell for this thesis. A computer crash required manual control and data acquisition for the experiments done with the four inch cell. An Agilent 3640A dc power supply was used for the electrodes. An analog dc power supply and multimeter were used for the sensor ring and the pressure transducer.

A voltage slightly higher than the voltage applied to the electrolysis electrodes is supplied to the sensor ring and it is monitored for amperage by the multimeter. The sensor ring serves three purposes; sense sulfur dioxide escaping the anode compartment, reject hydrogen ions to the cathode compartment and oxidize escaping sulfur dioxide before it leaves the cell.

Twelve volts dc is supplied to the pressure transducer with the analog power supply. An output voltage between 0 and 5 volts is read with the multimeter and multiplied by 30 to determine the pressure in the cell.

3.6 Experimental Results

Only one successful run was made with the four inch cell. Several seemingly unsuccessful runs did manage to prove that two of the design changes were successful. Unless there were issues with the flow system or pressure regulation, migration of sulfur dioxide to the cathode compartment had been deterred. There were several issues with pressure regulation in the unsuccessful runs, often resulting in excessive pressure, due to blocked pressure regulators. The new stand design and higher pressure rated glass resulted in no damage to the glass window.
The one successful run with the four inch cell implemented all of the changes discussed in section 3.1.2. It was deemed a success because it was the longest run with no sulfur dioxide diffusion to the cathode compartment.

It was the first run implementing the tungsten carbide electrodes. This design change was not deemed successful. A current voltage comparison chart is shown in figure 3.5. It compares the last run of Chettiar [12] to the run with tungsten carbide electrodes.

![Current Voltage Comparison](image)

**Figure 3.5 Current Voltage Curve Comparison**

The results at lower voltages look deceptively encouraging. Due to time constraints the current at the lower voltages was not allowed to settle to its lowest point as was later done at the higher voltages. Possibilities for the lower current with the tungsten carbide electrodes include the fact that platinum from the previous run is a better cathodic catalyst than tungsten carbide and much less anodic surface area due to much lower porosity of tungsten carbide than carbon.

Another drawback to the use of the tungsten carbide electrodes was the production of a purple substance. Oxides of cobalt and manganese are known to be blue to purple in color. Cobalt and manganese are known binders used to hold tungsten carbide compounds together. The electrodes were treated electrochemically, soaked in ambient temperature sulfuric acid for days and treated in boiling sulfuric acid for hours to attempt to leach out the binders to no avail.
It was hoped the leaching of the binder would eliminate contamination of the sulfuric acid with the oxide and increase porosity of the tungsten carbide. Sulfuric acid contamination did not noticeably diminish after extensive treatment nor did porosity noticeably increase. This led to the work investigating electrode materials and catalysts described in the following chapter.
CHAPTER 4

ELECTRODE AND CATALYST TESTING

4.1 Overview

Results from the work by Chettiar with the four inch cell and results from preliminary work for this thesis led to the decision to do some studies of electrode materials and catalyst deposition techniques before proceeding. All the previous work showed that the biggest apparent problem was with the anode material. All metals tested showed effects of corrosion on the anode when a potential was applied to the electrodes. It was believed a charge build up due to inhibited ion diffusion in porous carbon was a draw back to carbon electrodes. Carbon electrodes were still considered due to there extensive use in other research and commercial systems.

Literature reviews led to the decision to continue to try tungsten carbide and ruthenium oxide as catalysts [19] [20]. It was decided to attempt to try lead electrodes due to leads relatively low melting point (327.4 °C) and malleability. It was believed these attributes could lead to a successful way to attach tungsten carbide and ruthenium oxide mechanically to an electrode.

Gold is known to be resistant to sulfuric acid and this fact was proven by earlier work when gold was used on the carbon anode and showed no deterioration. To decrease the porosity of the anode it was decided to try gold deposition on 316 SS for a protective coating.

The ultimate goal of this research is to lower the voltage required for electrolysis low enough that the voltage can be supplied by single junction silicon solar cell. Due to the fact silicon will eventually be used it was decided to start testing its durability as an electrode in this corrosive environment. It was also decided to try different catalyst and metal deposition techniques as might be needed on the silicon substrate in the future.
4.2 Lead Electrodes

Lead electrodes were fabricated by melting lead shot in a combustion boat 100 mm long and 20 mm wide. The lead shot was melted under nitrogen to prevent oxidation. The first electrodes showed considerable dark gray to black residue. Wire brushing and melting repeatedly reduced the amount of dark gray to black residue. It was noted that the lead shot had the same residue.

The lead shot was soaked five minutes in aqua regia which is a mixture of concentrated hydrochloric acid and nitric acid in a 3 to 1 ratio. This treatment formed a white residue on the pellets that was removed by stirring in deionized water. If the pellets were exposed to air they turned gray. If the shot was not going to be immediately placed in tube furnace under nitrogen it was stored in 20% acetic acid to prevent oxidation. The treatment also reduced the residue on electrodes but did not eliminate it completely.

4.2.1 Catalyst Deposition

Prior to deposition lead electrodes were formed as described in the previous section. To deposit tungsten carbide approximately 0.3 grams of 99% pure 10 micron tungsten carbide from Sigma Aldrich was placed in the bottom of the same combustion boat as was used to make electrodes. It was then placed in tube furnace under nitrogen flow and heated to 300 °C to ensure the powder was dry. After removal from the tube furnace the tungsten carbide powder was spread across bottom of the boat and covered with the lead electrode made earlier. The tungsten carbide was placed at the bottom of the boat due to the fact its density 15,700 kg m$^{-3}$ is greater than that of lead at 11,340 kg m$^{-3}$.

The boat was then placed in the tube furnace which was then purged with nitrogen before the atmosphere was changed to hydrogen to ensure no oxidation and reduce any oxides already formed. The temperature was raised to 400 °C for approximately 1 hour to make certain the lead was completely melted. The temperature was then lowered slowly to 260 °C before the furnace was shut off and the atmosphere returned to nitrogen. This appeared to leave a fairly even coverage of tungsten carbide on one side of the lead electrode.
Ruthenium oxide 99.9% pure also from Sigma Aldrich was deposited in a similar manner to tungsten carbide. Ruthenium oxide is less dense than lead 7050 kg m\(^{-3}\) compared to 11340 kg m\(^{-3}\) respectively. There were concerns that spreading ruthenium oxide only on top of the electrode would not break the surface tension and stick to the lead. Ruthenium oxide, approximately 0.2 grams, was dried then half was placed in the bottom of the boat and the second half on top of the electrode. The boat was then placed in the tube furnace under hydrogen.

The temperature was raised to 500 °C for 45 minutes and lowered slowly to 260 °C before the oven was turned off. The hydrogen reduced the ruthenium oxide to ruthenium. This resulted in good adhesion. One side was totally covered and the other side showed approximately 1/3\(^{rd}\) coverage.

The following ruthenium oxide depositions were done under a nitrogen atmosphere to prevent the reduction of ruthenium oxide. The first deposition resulted in only approximately 1/8\(^{th}\) of one side of the electrode had ruthenium adhered to it. The next deposition resulted in total coverage on one side and approximately 1/3\(^{rd}\) coverage on the other just like the ruthenium deposition.

**4.2.2 Experimental Setup**

The experiments were carried out in a system of beakers set up to slow diffusion of sulfur dioxide diffusion from the anode to the cathode compartment. The anode beaker was 30 ml beaker filled with glass beads. The anode beaker was submerged in a larger cathode beaker.

The 30 ml anode beaker was filled to the 25 ml mark with glass beads and 20% sulfuric acid. Sulfur dioxide gas was then slowly bubbled into the 30 ml beaker for one hour using a micrometering valve. Saturation of sulfuric acid with sulfur dioxide was assumed. One of the lead electrodes described in the previous section was then drilled for attachment of a 316 SS electrical lead. The lead electrode with no deposition was wire brushed to remove any oxide. The 316 SS lead was attached and the electrode was place in the saturated sulfuric acid solution. The 30 ml beaker was then filled to capacity with glass beads.
The 30 ml beaker setup and an oversized carbon cathode was then placed in a 250 ml beaker see figure 4.1 The 250 ml beaker was the filled with 20% sulfuric acid to approximately 6.35 mm over the top of the 30 ml beaker to create an electrolyte bridge between the anode compartment and cathode compartment. There was no flow or stirring in this setup.

![Figure 4.1 Electrode Testing Apparatus](image)

### 4.2.3 Control and Data Acquisition

Voltage was supplied to the electrodes with an Agilent 3640A dc power supply. The power supply was controlled by a program written in a graphical programming language for Labview, a software package from National Instruments. The program was written to control two Agilent 3640A power supplies. The building blocks for the program are drivers for the Agilent 3640A downloaded from National Instrument’s website. The driver’s were written into the program to allow voltages and amperages to be constantly monitored from the desktop computer and constant manipulation of voltages from the computer if needed. The program also allowed data to be saved to a file that could be opened later for data analysis. A screen shot of the user interface and the block diagram can be seen in appendix A.

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Voltages were also monitored by a National Instruments graphical program receiving data from a NI PCI-4351 data acquisition card linked to a TBX-68T terminal block, see appendix A. The program reads voltages from the data acquisition devices. One part of the programs designed for use in the four inch cell monitors voltages supplied by a pressure transducer that monitors system pressure. The voltage is correlated to pressure within the program.

Several channels can be read for measuring several voltages or pressures if needed. Voltages and pressures are shown numerically and graphically. Data is sent to a file for later data analysis. Voltage is monitored by this second program to verify the output of the power supply program and due to a desire to monitor residual voltage after the power supplies are turned off and disconnected from the system. A screen shot of this user interface and the block diagram can also be seen in appendix A.

4.2.4 Experimental Results and Discussion

Experiments were run with the setup described in section 4.2.2. Voltage was applied and monitored using the systems in the previous section. Voltage was raised from 0.5 V dc to 1.5 V dc in 0.25 increments at similar time increments for each experiment. A plot of the results is shown in figure 4.2.

![Electrode Comparison](image)

**Figure 4.2 Lead Electrode Results**
The results are shown as voltage versus current density. Current density is the current as read by the power supply divided by the cross sectional area of the electrode. The active area of the anode, the smaller electrode, was used. The active area for the lead only electrode was considered to be both sides of the electrode. The active area of the tungsten carbide coated lead electrode was considered to be only one side of the electrode because an oxide covered the other side of the electrode. The active area of the ruthenium and ruthenium oxide coated lead electrodes was considered to be one side and 1/3rd of the other side with the other 2/3rds of one side covered with an oxide.

The ruthenium coated electrode showed the lowest amperage. The electrodes with ruthenium oxide and tungsten carbide showed better results at lower voltages. It is believed that this is due to the catalytic activity. The seemingly better results of the lead electrode at higher voltages are possibly due to the oxidation of lead not from sulfur dioxide oxidation to sulfuric acid.

Only the best results from the tests with lead have been presented. There were several issues with sporadic results, contamination of the surface of the lead and adhesion of the catalysts to the lead. These issues were in conflict with the reasoning for attempting to use lead electrodes therefore the tests with lead electrodes were abandoned.

4.3 Carbon Electrodes

To attempt to get away from corrosion issues it was decided to try carbon as a substrate for catalyst deposition. Electrodes were fabricated from a carbon sample donated by Asbury Carbons. Four inch by ½ inch electrodes ¼ inch thick were cut out of the sample. A hole was the drilled in the electrode to facilitate the connection of an electrical lead. The same experimental setup, control system and data acquisition system were used as with the experiments with lead.

4.3.1 Catalyst Deposition

It was decided to try deposition of ruthenium oxide on carbon electrodes. A sol-gel technique describe in an article by Constantinou et al in Catalysis Letters was used [21].
The article describes a typical sol-gel technique in which a precursor, usually a salt and in their case RuCl$_3$, is dissolved in a solvent. The solution is then placed on a substrate and the temperature is raised to evaporate the solvent. The sample is then calcined at high temperature.

Specifically for these experiments the ruthenium oxide was deposited as follows. Approximately 0.251 grams of RuCl$_3$ was placed in 10 ml Isopropanol. This was supposed to create a 0.121 M solution. This actually created a heterogeneous mixture with some of the RuCl$_3$ dissolving into solution but a lot of it remained as solid particles in the mixture. The mixture was painted on to the carbon electrodes. The electrodes were dried at 80 °C for approximately 45 minutes in a tube furnace exposed to outside air. The temperature was then slowly raised to 500 °C. The temperature was maintained for 1 hour. The set temperature is changed to 22 °C and the temperature was allowed to drop naturally.

4.3.2 Electrode Characterization

To determine if RuO$_2$ was successfully deposited the carbon electrodes were characterized using a Hitachi S-800 Scanning Electron Microscope to perform scanning electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS) on the sample. The Hitachi S-800 SEM is owned and maintained by the University of South Florida Nanomaterials and Nanomanufacturing Research Center. A photograph and specifications are in appendix B.

A brief description of SEM as depicted by Iowa State University College of Engineering Department of Materials Science and Engineering was adapted as follows [22]. A beam of electrons is generated by an electron gun. The system is run at high vacuum to ensure no interference of gas molecules with the instable electron beam and to prevent damage to the electron gun by reaction of gas molecules. The beam is attracted through an anode, condensed by a condenser lens and focused as a very fine point on the sample by an objective lens. Scan coils are energized and create a magnetic field which deflects the beam back and forth in a controlled pattern.
The electron beam hits the sample, producing secondary electrons, auger electrons, X-rays and back scattered electrons. The secondary electrons and the back scattered electrons are collected by detectors which convert them to a voltage and amplify them. The amplified voltage is applied to a grid of a cathode ray tube, CRT. This causes the intensity of a spot of light to change. The image consists of thousands of these spots of light of varying intensity. This corresponds to the topography of the sample.

A succinct definition of EDS was adapted from the University at Buffalo, School of Dental Medicine website [23]. As previously stated X-rays are emitted when the electron beam hits the sample. They are created by shell transitions created within the individual elements caused by the energy of the electron beam. Each X-ray has the has an energy level consistent with its shell level and parent element. Detection and measurement of this energy allows for elemental analysis. This system can also be used to map the surface of the sample and show the distribution of elements.

An SEM image of the sample is seen in figure 4.3. The EDS spectrum and elemental analysis are shown in figure 4.4.

Figure 4.3 SEM Image of Carbon Electrode with RuO₂ Deposition

A map of the surface of the carbon electrode was also taken to determine the distribution of elements. The map of Ru atoms is overlayed on the SEM image in figure 4.5 with Ru depicted in yellow. Figure 4.5 shows a fairly even distribution of Ru atoms.
Figure 4.6 then shows the map of Ru overlayed on the map of O\textsubscript{2} again with Ru depicted in yellow and O\textsubscript{2} depicted in green. This figure shows Ru and O\textsubscript{2} are evenly distributed therefore the Ru compound present is RuO\textsubscript{2}. The amount of Ru depicted in figures 4.4-4.6 is low because the electron beam of the Hitachi S-800 Scanning Electron Microscope does not have enough energy to disperse k shell Ru electrons. Therefore only l shell electron transitions are detected.

![EDS Spectrum](image)

**Figure 4.4 EDS Spectrum RuO\textsubscript{2} on C**

![SEM Image](image)

**Figure 4.5 SEM Image of Carbon Electrode with Ru Map Overlay**
4.3.3 Experimental Results and Discussion

The set up of the experiments with carbon was the same as the experiments with lead. The operation was slightly different. Only two voltages were used for these experiments. This was done to assure that water was not being directly decomposed. Each experiment was run for ½ hour at 0.5 volts then ½ hour at 1 volt. Ruthenium oxide was used as both an anodic catalyst and cathodic catalyst. Different combinations of carbon and ruthenium oxide coated electrodes with and with out sulfur dioxide were used. The results for carbon cathodes are plotted in figure 4.7. The results for ruthenium oxide coated cathodes are plotted in figure 4.8.

![Graph showing the comparison of carbon cathode results with and without sulfur dioxide.]

Figure 4.7 Carbon Electrode Results, Carbon Cathode
Figure 4.8 Carbon Electrode Results, RuO$_2$ Coated Cathode

Results appear to show catalytic activity for hydrogen evolution on the cathode as well as sulfuric acid production at the anode. A larger benefit appears to occur at the cathode. These results considered positive and led to further work with the sol-gel deposition technique for ruthenium oxide and carbon electrodes which will be discussed later.

4.4 Silicon Electrodes

In another attempt to stay away from corrosive metals silicon electrodes were tested. The electrodes were made from two inch n-Si 0.4-0.6 ohm-cm 0.55 mm thick and two inch p-Si 7.2-10.8 ohm-cm 0.55 mm thick. These were the lowest resistivity wafers the group had easy access to. Low resistivity wafers were desired to minimize voltage loss through the wafer. Voltage loss is calculated simply with Ohm’s Law, which is depicted in equation 20.

\[ V = IR \]  
\[ (20) \]

In equation 20 $V$ is voltage loss in volts, $I$ is current in amperes and $R$ is resistance in ohms. Resistance is calculated using the quoted resistivity of the material the current is being passed through using equation 21.

\[ R = \rho L A^{-1} \]  
\[ (21) \]

In this equation $R$ is again resistance in ohms, $\rho$ is resistivity in ohm-cm, $L$ is length in cm of the resistive path and $A$ is the cross sectional area of the resistive path in cm$^2$. 
The experiments and tests were set up to lower the resistance of the electrodes. Therefore they were set up to use the 2 inch face as the cross sectional area of the wafer and the 0.55 mm thickness as the length.

### 4.4.1 Cleaning

Critical to any deposition is the cleanliness of the substrate. This is important because it might not be known what effect the contaminants could have on adhesion of the material deposited. Even more critical for deposits on silicon where low resistance is desired is the removal of silicon dioxide from the surface. Silicon dioxide has resistivity in the range of $10^{12}$ to $10^{18}$ ohm-cm.

With resistivities as high as just stated, Angstroms of native oxide can cause considerable voltage loss through that layer. One angstrom of native oxide on a two inch wafer can result in an added resistance of 4930 ohms which correlates to a voltage loss of 493 volts. Fortunately due to impurities in the oxide layer and diffusion of metals used for contacts or catalysts the effects are not near as bad as possible with pure native oxide.

Initially wafers were cleaned with a very basic cleaning technique. They were rinsed with Acetone to clean organics and then soaked in 100:1 HF buffered oxide etch. The initial resistances measured were quite high. The cleaning process was considered as one of a few possible reasons for these high resistance measurements.

Another more detailed cleaning system was found on the website from Holon Institute of Technology in central Israel [24]. The procedure begins with a solvent clean with DI rinse. That step is followed by a RCA-1 clean with rinse. The procedure is concluded with a HF dip, DI rinse and blow dry.

The solvent clean uses two solvents because sometimes the acetone only treatment can leave a residue. The solvent clean is used to remove oils and organics from the surface of the wafer. The wafer is first placed in 55 °C acetone for 10 minutes. The wafer is then placed in ambient methanol for 2-3 minutes. After the methanol soak the wafer is soaked in DI and blown dry with nitrogen.
The RCA-1 process is so named because it was developed at RCA in the 1960’s by Werner Kern [25]. The solution for an RCA-1 clean consists of 5 parts water, 1 part 27% ammonium hydroxide and 1 part 30% hydrogen peroxide.

The RCA-1 process is also used to remove organics. The solution is prepared by first adding ammonium hydroxide to water and heating to approximately 70 °C. Hydrogen peroxide is then added to the solution. Once it bubbles for 1-2 minutes the solution is ready.

Once the solution is ready the wafer can be placed in the solution for 15 minutes. After the allotted time the wafer is removed to a beaker with overflowing DI water. After several changes of water the wafer should be removed under running DI water to deter organics on the surface of water from depositing on the wafer.

The last step is the HF dip. The hydrofluoric acid is mixed to a 2% solution with DI water. The wafer is placed in the HF solution for only 2 minutes. The wafer is removed from solution and rinsed under running DI. The wafer is then tested to see if the surface is hydrophobic. An oxide free surface is hydrophobic and water will bead on the surface.

4.4.2 Metal and Catalyst Deposition

The first deposition tried with silicon was the deposition of ruthenium oxide on the n-Si wafers. The sol-gel technique used with the carbon electrodes was also used with the n-Si wafers. The wafers were cleaned using the first cleaning technique described in the previous section.

The deposition technique was slightly changed for the ruthenium deposition on silicon. The deposition was performed in a nitrogen rich atmosphere. A nitrogen rich atmosphere was chosen in hopes to create a reaction with the silicon dioxide if there was not enough oxygen to react with all the ruthenium. It was hoped that the reaction depicted by equation 22 would occur.

\[
4\text{RuCl}_3 + 3\text{SiO}_2 + O_2 \rightarrow 4\text{RuO}_2 + 3\text{SiCl}_4
\] (22)
It was determined by XRD that RuO$_2$ was formed. The results will be shown in the results section. Much more study has to be done to determine if reaction 22 actually occurred.

After a 45 minute etch in the buffered oxide etch the wafers were immediately painted on both sides with the sol-gel solution. The wafer was placed in a tube furnace positioned vertically, see figure 4.9.

![Figure 4.9 Tube Furnace](image)

Due to the fact the diameter of the silicon wafer was the same as the largest diameter tube that could fit in our furnace no tube was used. An apparatus was made to suspend the wafer in the middle of the furnace, see figure 4.10.

![Figure 4.10 Wafer Holder](image)
The wafer was placed in the holder and suspended in the tube furnace. Nitrogen was turned on to flush the furnace. The set temperature of the furnace was slowly raised to 80 °C. The 80 °C set temperature was maintained for one hour. The temperature was then slowly raised to 335 °C. The temperature was chosen because it is just below the decomposition temperature of RuCl$_3$ 360°C. It was hoped that this would allow the RuCl$_3$ to react with the SiO$_2$ before decomposing. The 335 °C temperature was maintained for one hour.

The temperature was then raised from 335 °C to 385°C. This temperature was maintained for 30 minutes. The temperature was finally raised to 500 °C and maintained for 30 more minutes. The furnace was then allowed to cool naturally by lowering the set temperature to 22 °C.

Upon cooling the wafer was rinsed and scrubbed vigorously under DI, rinsed and scrubbed vigorously under Isopropanol and dried with nitrogen. This procedure was repeated up to 3 times per wafer.

The first metal depositions on silicon were done with a Hummer X Sputter Coater from the University of South Florida’s Nanomaterials & Nanomanufacturing Research Center (NNRC), see appendix B for pictures and specifications. At the time our main concern was resistance. The Hummer X was used due to its capability to ion etch prior to deposition. It was believed this could help reduce the resistance due to the native oxide formed immediately after chemical etching when the wafer is exposed to air.

The Hummer X has the capability to pump down to approximately 35 mtorr. This is not a very low vacuum pressure and allows for oxygen to be left in the chamber. Wafers were etched using the first cleaning procedure. A 60-70 nm layer of AuPd was deposited on both sides of multiple wafers. Some of the wafers were ion etched before deposition and some were not. The results displayed in figure 4.16 show the Hummer X AuPd depositions did not lower the resistance as low as desired. The AuPd also did not hold up to sulfuric acid. The Pd was attacked by the sulfuric acid and the AuPd flaked off the wafer.
The poor results with the Hummer X led to the use of another NNRC sputter system, the CRC 100 Sputter System by Plasma Sciences Inc, see appendix C for picture and specifications. This system was chosen due to its ability to reach higher vacuum, approximately 0.001 mtorr, and its ability to also ion etch. It was determined early on the system could not be used to ion etch due to the configuration used by NNRC.

Multiple wafers could be coated at the same time. Deposits were made on the n-Si and p-Si wafers described earlier. Wafers were prepared using the second more detailed cleaning procedure. A layer of approximately 2000 angstroms of silver was deposited on the side of the wafer that would not come in contact with sulfuric acid. A layer of approximately 100-200 angstroms of pt was deposited on the reactive side of the wafer. Results from this procedure show the best resistance results to date.

4.4.3 Electrode Characterization

To determine if RuO$_2$ was successfully deposited the silicon electrodes were characterized using the Hitachi S-800 Scanning Electron Microscope as described with the carbon electrodes. The SEM image is shown in figure 4.11. The EDS spectrum is shown in figure 4.12.

![Figure 4.11 SEM Image of Si Electrode with RuO$_2$ Deposition](image)
Figure 4.12 EDS Spectrum RuO$_2$ on Si

The EDS map of Ru overlaid on the EDS map of O$_2$ is shown in Figure 4.13 again with Ru depicted in yellow and O$_2$ depicted in green.

Figure 4.13 EDS Map of Ru on Si Electrode with EDS Map of O$_2$ on Si Overlay
It can be seen that the coverage of Ru is not consistent. \( \text{O}_2 \) appears more consistent due to the native oxide on the Si.

Further characterization of the RuO\(_2\) deposition on Si was carried out using the NNRC’s Panalytical X’Pert Diffractometer. A picture and specifications for the Diffractometer can be found in appendix B. A very brief description adapted from the Materials Analytical Services, Inc website follows [26].

X-ray Diffraction (XRD) is a powerful tool for characterizing crystalline materials. It is nondestructive to the sample. XRD provides information on structure, crystal orientation, crystallinity, etc. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam scattered from each set of lattice planes at specific angles. The X-ray diffraction pattern is a fingerprint of a specific material. When an X-ray pattern is taken of a sample the pattern can be compared to a data base to determine the makeup of crystals in the sample.

The results of the XRD of the RuO\(_2\) deposition on Si after multiple coats are shown in figure 4.14. Multiple layers show improved peak matching due the thicker coat. The vertical lines in figure 4.14 show the location of the literature values for the RuO\(_2\) [110] and [101] peaks.

![XRD Spectra for Sol-Gel RuO2 Deposition on Si](image)

**Figure 4.14 XRD Spectra for Sol-Gel RuO2 Deposition on Si**
4.4.4 Resistance Testing

The resistance was tested with an Agilent LCR meter. A jig was set up to maintain consistent pressure, see figure 4.15. The jig holds the wafer between two copper blocks. This setup was used instead of a four point probe system because multiple layers were going to be used on most materials. A four point probe system measures sheet resistance and is correlated to bulk resistance. It was determined with multiple layers this would not be a good approach.

![Resistance Test Jig](image)

**Figure 4.15 Resistance Test Jig**

4.4.5 Experimental Results and Discussion

Tests of RuO$_2$ deposition adhesion showed excellent adhesion. The wafers were scoured under DI water and Isopropanol with a neoprene glove. Adhesion was also tested with a tape test, where a piece of tape is placed on the wafer and removed to see if the deposited material will stick to the tape or the substrate. Long term tests of wafers coated in RuO$_2$ and placed in sulfuric acid show no visual change and no change in resistance. Results of resistance testing of wafers prepared under air and nitrogen rich atmospheres are shown in figure 4.16.
Deposits made by the Hummer X sputter system passed the tape test. It was noticed during setup for electrolysis the AuPd deposition was scraped off in places. As stated earlier the AuPd was attacked by sulfuric acid and peeled off the wafer. Results of resistance tests are shown in figure 4.16.

Deposits made by the CRC 100 sputter system showed excellent adhesion. The depositions passed the tape test and could not be scraped off. The wafers with Pt and Ag deposited with the CRC 100 sputter system showed the best results in resistances tests. Results are displayed in figure 4.16.

![Wafer Deposition Resistance](image)

**Figure 4.16 Resistance Test Results**

4.5 316 SS Electrodes

316 Stainless Steel electrodes were chosen early on because they were shown to hold up to sulfuric acid. They did not hold up when 316 SS was used as an anode. Considerable corrosion occurred with 316 SS anodes. Gold electroplating turned out to be a good seed layer for platinum depositions on cathodes, so it was decided to try gold plating of the anodes to inhibit corrosion.

4.5.1 Gold Plating

Acid Gold Strike by Technic Inc. was used as a seed layer for gold depositions also. Acid Gold Strike can only be used as a seed layer.
It is far too porous to be used as a protective coating and can only be applied at very limited thickness. Techni-Gold 25 E by Technic Inc. was plated on top of the seed layer to protect the 316 SS substrate.

316 SS was cleaned as previously reported by Chettiar [12]. The 316 SS was first cleaned with a detergent, Mean Green Industrial Strength cleaner. The electrodes were then soaked in 20 % NaOH-H\(_2\)O for approximately 10 minutes, rinsed with DI water and blow dried. They were then rinsed with 20 % HCl-H\(_2\)O, rinsed with DI water and blow dried.

Acid Gold Strike was first deposited. A carbon anode was used. The Acid Gold Strike solution temperature was maintained at approximately 90°F. The solution was stirred at medium speed. A current of 0.25 amps was maintained by varying voltage from 1.5 volts to 2 volts for approximately 2 minutes.

Techni-Gold 25-E was deposited immediately after Acid Gold Strike. A new carbon anode was used. The solution temperature was maintained at approximately 110°F. The solution was stirred at medium speed. A current of 0.04 amps was maintained by varying voltage from 0.46 volts - 0.6 volts for 30 minutes for cathodes and 90 minutes for anodes.

4.5.2 Catalyst Deposition

The thin layers of RuO\(_2\) deposits on silicon led to further investigation of literature concerning sol-gel RuO\(_2\) techniques. Upon further reading it was realized that most research was done with ruthenium chloride hydrate, RuCl\(_3\)-xH\(_2\)O dissolved in isopropanol as the precursor not RuCl\(_3\) [27] [28]. RuCl\(_3\)-xH\(_2\)O was ordered from Sigma Aldrich. Another source discussed dissolving RuCl\(_3\) in 20 % HCl and drying prior to dissolving in isopropanol [29]. This technique was attempted and the solution showed better solubility of the solid.

The first step in the new technique for preparing sol-gel solution was to grind 0.4355 g RuCl\(_3\) using a mortar and pestle. The RuCl\(_3\) was then dissolved in 20 % HCl. The solvent was boiled off and the RuCl\(_3\) was dried in an oven.
The solid is then dissolved in isopropanol and shows better solubility than non pretreated RuCl₃. The 0.121 M solution is still heterogeneous but much less solid settles out of solution. The same steps for calcining the RuCl₃ as used with silicon were followed.

The formed ruthenium oxide showed good adhesion. The deposits held up to cleaning in DI water and isopropanol. They also passed the tape tests. The new technique did not appear to improve the thickness of the layers. The catalytic affect of the deposits will be discussed in the next chapter on the two inch cell.

The final deposition technique used was sputter coating Pt on the gold plated electrodes in the CRC 100 sputter system. Pt had been successfully deposited on new electrodes and used electrodes that had been cleaned. The used electrode were first cleaned in toluene, dried and rinsed with DI water. The electrodes were then soaked in 20% NaOH for approximately 20 minutes followed by a DI water rinse and dry. The electrodes were finally rinsed with 20% HCl, DI water and then dried.

Once again a layer of approximately 100-200 angstroms of Pt was deposited. The deposition showed very good adhesion. It passed the tape test and could hold up to cleaning in DI and solvents.

4.5.3 Electrode Characterization

Characterization of the RuO₂ deposition on Au on 316 SS was carried out using the NNRC’s Panalytical X'Pert Diffractometer. The results of the XRD of the RuO₂ deposition on Au on 316 SS are shown in figure 4.17. The vertical lines in figure 4.17 show the location of the literature values for the RuO₂ [110] and [101] peaks.
Figure 4.17 XRD Spectra of RuO₂ Deposited on Au on 316 SS
CHAPTER 5

TWO-INCH ELECTRODE CELLS

5.1 Overview

The deposition techniques from the previous chapter had a large part in the decision to develop the two inch electrode cell. Some of the equipment available to our group for deposition had size limitations. Another determining factor was the availability of supplies. The housing of the two inch cell was polycarbonate. Polycarbonate has only a fair rating with sulfuric acid but it is much easier to pick up locally and can take the place of both Teflon and glass because it is clear. The gasket material was changed from Viton to EPDM also because of local availability. Other design issues will be discussed in the individual sections where they were implemented either the liquid electrolyte cell or the solid electrolyte cell.

5.2 Liquid Electrolyte Cells

The two inch electrode liquid electrolyte cells were designed with knowledge gained from operating the 4 inch electrode cell. They were developed to try a benefit from the lower conductivity of aqueous sulfuric acid than Nafion. The liquid electrolyte cells were designed with one main similarity to the four inch diameter electrode cell. They were built to facilitate an easy conversion to a solar chemical cell. They were built so the electrodes could easily be replaced by a 2 inch silicon wafer designed as a solar cell. The first liquid electrolyte cell was run at ambient temperature and pressure. The second liquid electrolyte cell was run at ambient temperature and approximately 90 psig.

5.2.1 Design Considerations

The cell was built with limited volume to force the reactants against the electrode, especially in the anode compartment.
The anode compartment was packed with carbon fiber to create more surface area and further reduce cell volume. See appendix C for 2 dimensional drawings.

The electrolyte bridge was placed to give sulfur dioxide entering the anode compartment the longest path length possible to the cathode compartment, see figure 5.1. Due to the possibility that all the sulfur dioxide might not be electrolyzed, the outlet was placed lower than the electrolyte bridge and a flow gradient was maintained from the cathode compartment to the anode compartment to keep sulfur dioxide from entering the cathode compartment and sweep unreacted sulfur dioxide out with the product acid.

Figure 5.1 Two-Inch Low Pressure Liquid Electrolyte Cell

In the low pressure cell the electrodes were made to extend beyond the bottom of the cell so electrical connection can be made outside of the cell so corrosion is not an issue. The gold plated 316 SS electrodes are placed back to back and insulated from one another and sealed with apiezon grease. When silicon electrodes are used copper current collectors are pressed to the back side of each electrode and extended outside of the cell.
The current collectors are insulated from each other with a thin sheet of Teflon. The backside of the electrodes and current collectors are sealed from sulfuric acid by EPDM rubber.

The 80 psig cell needed some design changes to prevent leaks. The entire cell body and gaskets were extended to from 4” X 4” to 4” X 6” to facilitate extra bolts at the bottom and top of the cell. See appendix C for 2 dimensional drawings of each section of both cells. The electrodes were expanded from 2” X 4” to 4” X 4” to allow for more gasket and electrode contact area to stop leaks. The 80 psig cell can be seen in figure 5.2.

Figure 5.2 Two-Inch 80 psig Liquid Electrolyte Cell
5.2.2 Flow System/Operation

The flow is considerably less complex for the two inch liquid electrolyte cell than the 4 inch diameter electrode cell, see figure 5.3. A big part of lowering the complexity is the use of gaseous SO$_2$ to saturate the acid entering the anode compartment instead of pumping liquid SO$_2$ directly into the cell. This makes it possible to operate at a lower pressure. Previously the cell was operated at 100 psi to assure the liquid SO$_2$ did not flash from rapid pressure drop and expand rapidly to vapor causing valves or fittings to freeze up. This low pressure operation was later changed due to some minor separation of dissolved SO$_2$ to form gas bubbles that increased the likelihood of SO$_2$ migration to the cathode compartment. Difficulties also arose from the low pressure SO$_2$ coming out of solution before the pump causing the pump to lose prime and stop pumping.

The 30% sulfuric acid was saturated with SO$_2$ prior to operation by bubbling SO$_2$ into a container of sulfuric acid. Several inches of water column pressure are maintained by allowing enough gas pressure to push several inches of sulfuric acid up the vent tube. Saturation is assured when several inches of water column pressure is maintained for several hours, because if pressure dropped SO$_2$ was being absorbed. The vent tube was closed in the 80 psig experiments to maintain a saturation cell pressure equal to the vapor pressure of SO$_2$, approximately 35 psig. Saturation is assured when the system equalizes at the vapor pressure of SO$_2$ and the SO$_2$ gas feed no longer bubbles into the pressurized cell. Positive pressure is maintained during electrolysis by slowly bubbling SO$_2$ into solution through the micro metering valve V-1 while the SO$_2$ pump is pumping.

After saturation is assured the electrolyzer is placed in the system. To fill the electrolyzer with electrolyte valves V-2 and V-3 are opened and the catholyte pump is turned on to approximately 1 ml/min. Once the electrolyzer is full, sulfuric acid will come out into the product acid tank. During 80 psig operation a 80 psig back pressure regulator is placed in line at the product acid tank to maintain pressure in the cell. The catholyte pump can be turned back to the operating pump rate of 0.03 ml/min. The gas pocket at the top of the cathode compartment is maintained by manipulating valve V-8 and the catholyte pump rate if needed.
Figure 5.3 PFD for Two-Inch Liquid Electrolyte System

Once the electrolyzer is full, voltage can be applied to the electrodes. The same control and data acquisition system are used as was described in section 4.2.3. Once a potential difference is across the electrodes SO$_2$ can be introduced to the anode compartment. Valves V-4 and V-5 are turned on and the SO$_2$ pump is turned on to 0.01 ml/min.

Upon completion of the electrolysis run the system can be switched to water for rinsing the system. It is best to maintain a potential difference across the electrode when the system is being cleaned. It provides extra time to oxidize SO$_2$ in the system. The first step towards shutdown is to close valve V-4 and open valve V-6. This allows water to enter the anode chamber.

After considerable drop in amperage it is ok to rinse the entire system. To do this valve V-2 is closed and valve V-7 is opened. After amperage is nearly nonexistent the control system can be shut down. The pump rate of both pumps can be increased to 1 ml/min each, to decrease rinsing time. Typically 250 ml is pumped through each pump to assure the pumps and the system are clean.
5.3 Solid Electrolyte Cell

Work was started with solid polymer electrolyte because it has been reported that solid polymer cells were successfully used in the past [13] [19]. Processes have been borrowed from the manufacture of typical PEM electrolyzers used for electrolyzing water. Certain design changes had to be made to make PEM style electrolyzers work.

5.3.1 Design Considerations

The biggest issue with using solid polymer electrolyte is the diffusion of \( \text{SO}_2 \) through the electrolyte. A key in determining how conductive a solid polymer will be is the amount of water uptake in the matrix of the polymer. This causes problems with sulfur dioxide because sulfur dioxide is very soluble in water and diffuses very quickly through water. This ability for rapid diffusion is defeated in the liquid electrolyte cell with a flow gradient against the diffusion. Convective transport of sulfuric acid in the liquid electrolyte cell is able to overcome the diffusive transport of sulfur dioxide.

Nafion® is not porous. It holds its water trapped in the matrix. There is no flow. Therefore this was overcome by the addition of a third cell. Sulfur dioxide is allowed to diffuse through the first layer of Nafion® where it is met by a perpendicular flow through the center compartment rapid enough to convectively sweep away the \( \text{SO}_2 \) before it can diffuse through that central compartment, see figure 5.4. This can be accomplished because the rate of diffusion of hydrogen ions in sulfuric acid is much greater than the rate of diffusion of sulfur dioxide. Hydrogen Ions diffuse through the center compartment rather than being swept away like \( \text{SO}_2 \).

Electrodes for PEM electrolyzers are considerably different. The porous electrodes along with catalysts are mechanically pressed and stuck to the membrane creating one cohesive unit called a membrane electrode assembly (MEA). MEA design and manufacture will be discussed in the next section.

With the actual electrode attached to the membrane this leaves what in the liquid electrolyte cell is considered an electrode to be a current collector, a means to pass current (electrons) to the actual electrode.
The anode current collector has two holes, see figure 5.4. The bottom one allows the reactants to enter the small anode chamber packed with carbon the makes the electrical contact to the electrode that is pressed to the solid electrolyte. The reactants are forced by flow to the reactive interface where the electrode and catalyst contact the solid electrolyte. The top hole in the current collector allows the product acid and any unreacted material to exit the cell.

The cathode current collector has several holes to allow hydrogen, created at the interface of the solid electrolyte and porous electrode, to escape. Some experiments the cathode compartment from a water electrolysis cell designed by Heliocentris was used. The borrowed parts included the housing, current collector, and MEA.

![Figure 5.4 Three Compartment Solid Electrolyte Cell](image)

The center compartment is simply two pieces of EPDM with capillary tubes sealed in packed with glass fiber.
The EPDM center compartment serves as the seal to seal each MEA to its respective current collector. Sulfuric acid is passed through the capillary tubes creating the perpendicular convective flow described.

5.3.2 MEA Development

MEAs were produced similar to what is typically discussed in literature [30] [31]. Catalyst inks which in this case are a combination of Liquion™ LQ-1005 Nafion® solution from Ion Power, Inc and Ruthenium oxide 99.9% pure from Sigma Aldrich, 99% pure 10 micron tungsten carbide also from Sigma Aldrich or 5% Pt on activated carbon are air brushed or painted on 1.5” Teflon blanks. The inks are allowed to dry on the Teflon blanks. Typically the inks are hot pressed on both sides of a piece of Nafion®. In this case only one side is hot pressed because one side is a reactive surface and the other is the center compartment where no reaction takes place.

Nafion® membrane N112 is cleaned by ½ hour in boiling and stirred 3% hydrogen peroxide, ½ hour in boiling and stirred DI water and ½ hour in boiling and stirred 0.5M sulfuric acid. The membrane is dried in a 200 C oven for two minutes.

The Nafion® membrane and coated Teflon blank are pressed between two preheated 2” diameter copper blocks protected by 2.5” diameter Teflon. The copper blocks are preheated to 200 C. The system is stacked as per figure 5.5 and hot pressed at 1000 psi for 2 minutes.

![Figure 5.5 Membrane Hot Press Diagram](image_url)
Upon cooling the system is disassembled. The result of this process is the catalyst and electrode material on the Teflon blank are transferred to the Nafion®.

5.3.3 Flow System/Operation

The process flow diagram for the 3 compartment system is depicted in figure 5.6. The saturation system works the same for the three compartment system as it does for the 2 inch liquid electrolyte system. The cathode compartment in the three compartment system no longer has flow. The first step after saturation is to fill the cathode compartment. The cathode compartment is filled with a syringe. The second step is to open valves V-2 and V-3 and run the center compartment pump at 1ml/min.

![Figure 5.6 PFD for 3 Compartment Cell](image)

Once flow is running through the center compartment the voltage can be applied to the electrodes. After there is voltage to the electrodes valves V-4 and V-5 can be opened and the SO\textsubscript{2} pump started at 0.01 ml/min.

Upon completion of the electrolysis run the system can be switched to water for rinsing the system. It is best to maintain a potential difference across the electrode when the system is being cleaned. It provides extra time to oxidize SO\textsubscript{2} in the system.
The first step towards shutdown is to close valve V-4 and open valve V-6. This allows water to enter the anode chamber.

After considerable drop in amperage it is ok to rinse the entire system. To do this valve V-2 is closed and valve V-7 is opened. After amperage is nearly nonexistent the control system can be shut down. The pump rate of both pumps can be increased to 1 ml/min each, to decrease rinsing time. Typically 250 ml is pumped through each pump to assure the pumps and the system are clean.

5.3.4 Monitoring Sulfur Dioxide Diffusion

It is important that sulfur dioxide does not diffuse to the cathode compartment. Sulfur is known to poison cathode catalysts especially when Pt is used. Sulfur is one of the possible products when SO$_2$ is reduced. Another possible product is H$_2$S. H$_2$S is a deadly gas. It is not desired to have such a dangerous in the product.

The center compartment acid and the cathode compartment acid are closely monitored in this three compartment setup. Samples are taken from the center compartment and cathode compartment during operation. The samples are placed in a 1 mm path length cuvette and absorbance is measured in an Ocean Optics UV-VIS system. This system is used because SO$_2$ has high absorbance in this light range and sulfuric acid and water do not.

5.4 Goals and Limitations

The ultimate goal of this research is to solar chemical hydrogen production. This sets a limitation for the research. The max solar insulation is 1000 watts/m$^2$. If we rather grandly assume 10 % efficiency this becomes 100 watts/m$^2$ of available power. Conversion to cm$^2$ gives .01 watts/cm$^2$. We now consider the equation for power as seen in equation 23.

$$P = V \times I$$  \hspace{1cm} (23)

P in this case is the power density in watts/cm$^2$. V is the voltage in volts and I in this case is the current density in amps/cm$^2$. 

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The target voltage for a single junction silicon solar cell is 0.5 volts and for a CdTe cell is 0.7 volts. Plugging these numbers and the maximum possible power density into equation 23 leaves a max current density of 0.014-.02 A/cm².

Another limitation to the max current density is the choice to use SO₂ saturated H₂SO₄ at ambient pressure to deliver the reactants to the cell. The amount of reaction governs the current density in an electrochemical cell. The amount of reactants can limit the amount of reaction. Therefore we need to know how much limiting reactant is getting to the cell at the experimental flow rate.

The acid concentration used for maximum conductivity is 30%. Solubility data for SO₂ in 30% H₂SO₄ was reported by Hayduk [29]. The solubility of SO₂ in 30% H₂SO₄ is approximately 0.105 g/g. A current density at the operating flow rate can now be calculated assuming negligible volume change of the solvent when saturated.

The operating flow rate for the anode compartment in the experiments is 0.01 ml/min. The density of 30% H₂SO₄ is 1.219 g/ml. Therefore the mass flow rate is 0.0129 g/min. This makes the mass flow rate of SO₂ in the approximately 0.00136 g/min. These flow rates now have to be converted to moles/sec so Faraday’s law can be used to determine the current.

The molar flow rate is 3.53 x 10⁻⁷ mol/sec. Faraday’s law is given in equation 24.

\[ n = \frac{I}{z \times F} \]  (24)

In this case because SO₂ and H₂ are equamolar \( n \) is the moles of SO₂. The letter \( I \) is the current given in amps which is also known as coulombs/sec. The letter \( z \) is the number of moles of electrons per mole product, in this case 2. Finally \( F \) is the number of coulombs per mole of electrons or approximately 96500. Equation 24 can be rearranged and solved for the current. The total current is 67.5 mA. The current divided by our electrode area gives the current density. The current density max limit due to SO₂ is approximately 5.0 mA/cm² at the experimental flow rate.

5.5 Experimental Results and Discussion of Preliminary Experiments

A main concern of both designs for two inch electrodes was to deter the diffusion of SO2 to the cathode compartment. That design goal was achieved.
The experiments discussed in this section had run times varying from 30 minutes to 5 hours with the average being approximately 2 hours. There was never any evidence that SO₂ was in the cathode compartment.

5.5.1 Experiment 1

The first experiment was run using the liquid electrolyte cell as depicted in figure 5.1. The cathode was gold plated 316 SS. The anode was gold plated 316 SS with RuO₂ deposited as describe in section 4.5.2. RuO₂ was not used on the cathode because tests performed in beakers showed poor adhesion of RuO₂ after electrolysis despite seeming mechanically sound before electrolysis. As figure 5.7 shows this is the poorest results of any of the liquid electrolyte experiments. The anode had been used before and the RuO₂ was a little depleted. After experiment 2 it was determined the RuO₂ adhesion was suspet on the anode after electrolysis.

5.5.2 Experiment 2

The second experiment followed immediately after the first. The same configuration was used except the anode compartment was packed with carbon fiber. As can be seen in figure 5.7 this greatly improved the current density. This is more than likely due to the extra surface rather than increased flow rate through lower volume compartment. This has been determined because increased flow velocity through the same volume does not show as much benefit as is produced here. The current density is increase by greater than a factor of 5 through use of the anode carbon. Upon disassembly of the cell it was noted that more of the RuO₂ has come off of the electrode. Despite good adhesion prior to electrolysis, it appears that both the cathode and anode RuO₂ deposits are adversely affected by electrolysis.

5.5.3 Experiment 3

The third experiment was also done in the liquid electrolyte cell and was set up as described in section 5.2.1.
This experiment used Pt on an n-Si wafer for the cathode and Pt on a p-Si wafer for the anode. The results can be seen in figure 5.7. It showed one of the best results at higher voltage. There were some minor adhesion issues with the Pt on Si after electrolysis. It is believed they were caused by the sealing grease used. It was also apparent upon disassembly that the sealant between the electrodes was not sufficient and the Ag backside contacts were affected by the sulfuric acid.

5.5.4 Experiment 4
The fourth experiment was set up the same as the third except the electrode assembly was sealed with liquid EPDM and allowed to cure for several days. It showed the most promising result at lower voltage as can be seen in figure 5.7. This is promising for the long term research because ultimately Pt on silicon will serve as the Schottky barrier and cathodic catalyst in the solar chemical cell. A comparison can not be made to experiment 3 because that experiment was only done at high voltage.

5.5.5 Experiment 5
For the fifth experiment it was decided to get a baseline experiment with no catalyst. This was another liquid electrolyte experiment. It was again set up as figure 5.1 depicts. This was the longest run. It was the best proof that the diffusion problem with SO₂ has been solved. As was expected this setup shows the lowest current density of the liquid electrolyte cells so far excluding the first experiment which is the only run with out carbon packed in the anode compartment.

5.5.6 Experiment 6
The sixth experiment is the first solid electrolyte three compartment cell experiment. It is also the only one presented that is assembled exactly as is depicted in figure 5.4. The MEAs both have 5% Pt on activated carbon electrodes hot pressed as described in section 5.3.2. This was the longest 3 compartment run at 2.5 hours. It showed no diffusion of SO₂ through the second layer of membrane. This is the only experiment that showed a benefit from increasing the flow rate.
The flow rate to the anode was increased by a factor of 8 which increased the current by a factor of 7. The other experiments all showed little to no effect when the flow rate was increased.

![Preliminary I vs V Curves](image)

**Figure 5.7 Preliminary Two-Inch Cell Comparison**

### 5.5.7 Experiments 7-9

Experiments 7-9 have been lumped together because there is relatively small changes between them. All three experiments utilize gold plate 316 SS electrodes with 100-200 angstroms Pt deposited on them as described in section 4.5.2. The cell design is slightly changed between experiments 7 and 8 from that depicted in figure 5.1. A spacer was added to enlarge the cathode compartment because excessive bubble growth in experiment covered the cathode and blocked part of the electrolyte bridge.

It is reasoned that the current density drop from experiment 7 to experiment 8 is cause by a contaminated and depleted Pt surface.
At the end of experiment 7 valves were manipulated to try to improve hydrogen bubble evolution. This changed the flow in the system and SO\textsubscript{2} diffused into the cathode compartment. The SO\textsubscript{2} was reduced and sulfur was deposited on the cathode. In an attempt to clean the sulfur some of the catalyst was removed.

Experiment 9 seems to confirm the assumptions about changes from experiment 7 to experiment 8. The cathode from experiments 8 and 9 was thoroughly cleaned and a new deposition of Pt was done. This in combination with the larger cathode compartment gave the best current density results of this work.

5.5.8 Experiments 10 and 11

Once again experiments are lumped together for discussion due to their similarities. These experiments were run from a hybrid cell that was a combination of a commercial water electrolyzer designed by Heliocentris and design concepts from section 5.3.1, see figure 5.8. The commercial cathode compartment and catalyst were used in conjunction with a center compartment and anode similar to the ones depicted in figure 5.1.

![Figure 5.8 Hybrid 3 Compartment Cell](image)

As can be seen in figure 5.7 slightly better current densities were recorded but at a higher voltage than for the other three compartment cell experiment.
5.5.9 Conclusions from Preliminary Experiments

It was decided from the results and discussion of the preliminary experiments that a stringent enough scientific method was not followed. Even with this decision the preliminary results did allow for a narrower set of experiments to be set up that would allow more ease to follow a rigid methodology.

All three experiments with the three compartment cell resulted in much lower current densities than the liquid electrolyte cell excluding the experiment 1 that had much less anode surface area. It was determined from these results that no more three compartment cell experiments would be run.

As discussed in sections 5.5.1 and 5.5.2 there is an issue with RuO₂ adhesion during electrolysis. It was decided to not proceed with RuO₂ experiments at this time.

Sputtered Pt seems to be the only successful deposition technique at this time. It was determined the rest of the experiments would be run with Pt as the cathodic and anodic catalyst. The Pt on gold plated 316 SS are the sturdiest electrodes and easiest to seal. It was decided to run the majority of the experiments with the 316 SS electrodes until an optimum was determined then change to Pt on Si to make a final comparison.

5.6 Experimental Results and Discussion of Final Experiments

The final experiments were run following a much more rigorous scientific method. The experiments were run for much longer times and were not stopped unless some mishap with the flow system allowed SO₂ to diffuse to the cathode compartment. The experiments were run until the amperage from the cell leveled off for several minutes. This was done because when voltage is applied or raised the current typically spikes because the system is thrown out of equilibrium. Therefore, time must be allowed for the system to return to equilibrium.

These experiments again proved, barring mishaps, SO₂ diffusion has been eliminated. These experiments ran for 12-50 hours. The only time sulfur diffused to the cathode compartment was when the flow system was disrupted or if anode packing material shifted allowing a straight path to the cathode compartment for SO₂.
The only drastic change was a decision to run at higher pressure. This allows for a higher concentration of SO₂ but the results still show explainable trends. The first experiment was run at atmospheric pressure and the H₂SO₄ was saturated at only a few inches of water column pressure. The remainder of the experiments were run at approximately 70 psig and the H₂SO₄ was saturated at the vapor pressure of SO₂, approximately 35 psig. This should cause approximately a 2.4 times increase in SO₂ solubility according to literature [32].

5.6.1 Experiment 1

Experiment one was run similar to the preliminary experiments. It was run at atmospheric pressure. The flow rate to the anode was 0.1 ml/min. The flow rate to the cathode was 0.3 ml/min. It was run with the cell depicted in figure 5.1. The electrodes were 2” x 4” Pt on gold plated 316 SS electrodes. There was one anode and one cathode. The anode compartment was packed with 5 pieces of carbon fiber that was gold plated with orostrike plating solution. The fibers also had a 100-200 angstrom coat of Pt for catalytic effect. This run was considered the baseline run for comparison to the remainder of the final experiments. The results of this experiment can be seen in figure 5.9.

Difficulty was had maintaining prime in the SO₂ saturated H₂SO₄ pump due to bubble formation in the inlet line to the pump. An occasional bubble was noticed coming from the anode compartment. It was assumed the bubble was SO₂ because bubbles could also be seen coming out of the back pressure regulator in the inlet line to the cell. For this reason the remainder of the experiments were run at approximately 80 psig and the H₂SO₄ was saturated at the vapor pressure of SO₂, approximately 35 psig.

5.6.2 Experiment 2

Experiment two required the changes explained in the previous section. The raise in pressure caused leaks so larger electrodes were designed to assure more surface area for contact with gaskets in hope to stop leaks. Also clamps were added at the top and bottom of the cell where there were no bolts.
The active area of the electrode was not changed because the extra surface area was covered by gasket material. With the help of some clamps the leaks were stopped. The cell for this run was actually a combination of figure 5.1 and 5.2. The large electrodes from figure 5.2 were used in the cell depicted by figure 5.1.

The planned change for this run was to double the surface of the anode by adding a second anode. The same 5 pieces of Pt and Au coated carbon fiber were used to pack the compartment between the electrodes. Figure 5.9 and figure 5.10 show that little benefit was gained from doubling the anode surface area.

5.6.3 Experiment 3

Experiment 3 was run with the same cell design described for experiment 2. Instead of two anodes two cathodes were used. The cathode compartment was packed with the Pt and Au coated carbon fiber and the anode was packed with Au coated fiber.

Total current for this run was similar to the previous runs as seen in figure 5.9. Figure 5.10 shows current density calculated for hydrogen production. There is a significant drop in current density because the surface area of the cathode doubled. This shows the anode reaction is limiting the current.

Manipulating the anode surface area in experiment 2 showed little change in current density. This shows the system is not reaction rate limited. At the end of each experiment the flow rates were manipulated and showed only minor changes in current density. This seems to suggest the system is not reactant diffusion limited. This led to a decision to manipulate the electrolyte bridge to increase ion diffusion. The electrolyte bridge is restricted by the narrowness of the anode compartment. This was done to assure shorter diffusion path for reactants and restrict diffusion of SO₂ to the cathode compartment.

5.6.4 Experiment 4

As stated at the end of the last section it was decided to manipulate the restriction in the electrolyte bridge caused by the narrowness of the anode compartment.
This was done for this experiment by changing the thickness of the anode gasket. The anode gasket was changed from approximately 0.04 inches to 0.125 inches.

**Figure 5.9 Total Current vs. Voltage Curves: Experiments 1 Through 4**

**Figure 5.10 Current Density vs Voltage Curves: Experiments 1 Through 4**
Along with the change in anode gasket changes in cell design were implemented because one of the end plates was cracked during the last run. Thicker polycarbonate was used and the height of the end plates and gaskets were increased so the clamps in experiments 2 and 3 could be replaced by bolts. The same electrodes as experiments 2 and 3 were used. This cell is depicted in figure 5.2.

The added thickness of the anode compartment required additional carbon fiber to be placed in the anode compartment to restrict SO₂ diffusion. Because the thickness of the anode compartment was tripled the flow from the cathode compartment was tripled from 0.3 ml per minute to 0.9 ml/min to maintain the same cross sectional flow to inhibit SO₂ diffusion. For the purpose of limited change no more Pt was added to the carbon fibers. The fibers were gold plated to improve conductivity. The thicker anode compartment showed improved current density, see figure 5.9. This seemed to confirm the assumption that the narrowness of the electrolyte bridge restricting ion diffusion is the rate determining step.

It was decided to enlarge the anode compartment again for the next experiment. The results from experiment three can also be seen as the base line for figure 5.10.

5.6.5 Experiment 5

Manipulations of flow rates at the end experiment 4 showed that the increased flow from the cathode was probably not need, but for consistency and safety from SO₂ diffusion 0.9 ml/min will be maintained for the remainder of the experiments but further increases were not deemed necessary. The anode compartment was enlarged from experiment 4 by changing from the 0.125 inch gasket to a 0.25 inch gasket. Additional carbon fiber was gold plated and added to the anode compartment.

The larger anode compartment again proved beneficial. The results can be seen in figure 5.10. The restriction from ion diffusion seemed to be lessened so it was decided to again try to manipulate the surface area.
5.6.6 Experiment 6

A second anode was added to the outside of the anode compartment for experiment 6. The same carbon fiber packing material from experiment 5 was used except one Pt coated piece was lost and replaced with a gold plated piece. This time increasing the anode surface area showed improvement as can be seen in figure 5.10. This shows that sulfuric acid production is the rate limiting reaction.

5.6.7 Experiment 7

A second cathode was added to the outside of the cathode compartment for experiment 7. The rest of the setup is the same as experiment 6. The total current went up as seen in figure 5.11, but the current density calculated for hydrogen production actually went down as shown in figure 5.12. This confirms the findings of experiment 6 that the anode reaction seems to be the limiting reaction. Another limiting factor for this run is the fact that for the first time all the SO₂ being pumped in to the cell is being used up at the highest voltage.

The current of 71.18 is higher than the current possible at the flow rate due to solubility limits because the concentration is higher than what is being pumped in due to unreacted SO₂ from lower voltages and currents. This means the system is relying more on SO₂ diffusion than the convective flow from the input pump rate.

This will most likely cause uneven current distribution on the electrode. Once all excess SO₂ is used up the current will eventually drop to 67.5 if the solubility data is correct. This will cause very uneven current distribution because no SO₂ will make it to the top of the electrode because it will all be reacted before it gets there.

5.6.8 Experiment 8

It was decided to try packing the cathode compartment with gold plated carbon to increase the linear flow through the compartment to hopefully sweep sulfate and bisulfate ions and hydrogen away from the cathode and hopefully help hydrogen ion diffusion to the cathode surface. The Pt coated carbon was placed in the cathode compartment because it is a better hydrogen catalyst than sulfuric acid catalyst.
Total current was slightly lower, see figure 5.11, probably due to more difficulty with hydrogen evolution due to the carbon packed compartment. The same restriction at 1.2 volts from higher amperage and complete electrolysis of input SO$_2$ as experiment 7 will hold.

Figure 5.11 Total Current vs Voltage Curves: Experiments 4 Through 8

Figure 5.12 Current Density vs Voltage Curves: Experiments 4 Through 8
5.6.9 Experiment 9

Experiment 9 was run to give a base line for the cell with out the use of SO$_2$ to lower the voltage requirement for hydrogen production. This experiment was run with the same setup as experiment 6. The results were as expected with very low current density because the cell was operated at the same voltages which are too low for direct dissociation of water. The results can be seen in figure 5.13.

5.6.10 Experiment 10

The anode compartment was expanded from 0.25 inches to 0.58 inches for this experiment by changing the 0.25 inch gasket to two 0.04 inch gaskets, one on either side of a 0.5 inch piece of polycarbonate. Another piece of Pt coated carbon fiber was lost, so the system was run with only three pieces of Pt and Au coated carbon fiber sheets and 70 Au coated carbon fiber sheets. The highest currents to date resulted and are compared to experiments 6, 9 and 11 in figure 5.13 and current densities in figure 5.14.

![Current vs Voltage](image)

**Figure 5.13 Total Current vs Voltage Curves: Experiments 6 and 9 Through 11**

Once again the max current due to input flow was topped at higher voltages. With this experiment it started at 1.1 volts. Once again this means the system was relying on unreacted SO$_2$ from lower voltages and amperages.
To further test the expansion of the cross sectional area of the electrolyte bridge the cell will need to be redesigned. The cross sectional area of the electrolyte bridge is now consistent from cathode to anode so both compartments and the height of acid above the electrodes will need to be changed. It was decided to run the final run with this design with silicon electrodes with the same 100 to 100 angstrom deposition of Pt on the anode and cathode.

![Current Density vs Voltage](image)

**Figure 5.14 Current Density vs Voltage Curves: Experiments 6 and 9 Through 11**

### 5.6.11 Experiment 11

As stated above this experiment was run with Pt coated Si electrodes. The back side was coated with silver to improve conductivity. The Si electrodes were sealed to the electrodes from the previous runs with apiezon wax. Current density went down from experiment 9 as can be seen in figure 5.11. It was noticed that hydrogen bubbles grew much larger on the Si electrodes than the gold plated 316 SS electrodes. This could have inhibited current because the hydrogen bubbles become an insulator against ion flow. As with experiments 7, 8 and 10 the system was restricted at higher voltages. This time like experiment 10 the high amperages were at 1.1 volts and 1.2 volts. Below is a table which summarizes all the final experiments.
### Table 5.1 Experimental Parameter Comparison

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Exp. 1</th>
<th>Exp. 2</th>
<th>Exp. 3</th>
<th>Exp. 4</th>
<th>Exp. 5</th>
<th>Exp. 6</th>
<th>Exp. 7</th>
<th>Exp. 8</th>
<th>Exp. 9</th>
<th>Exp. 10</th>
<th>Exp. 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (psig)</td>
<td>0</td>
<td>~80</td>
<td>~80</td>
<td>~80</td>
<td>~80</td>
<td>~80</td>
<td>~80</td>
<td>~80</td>
<td>~80</td>
<td>~80</td>
<td>~80</td>
</tr>
<tr>
<td>Flow Rate (ml/min)</td>
<td>0.01</td>
<td>0.010</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Anode Thickness (in)</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.125</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Anode Packing</td>
<td>5 Pt</td>
<td>5 Pt</td>
<td>5 Au</td>
<td>5 Pt</td>
<td>5 Pt</td>
<td>5 Pt</td>
<td>5 Pt</td>
<td>5 Pt</td>
<td>5 Pt</td>
<td>4 Pt</td>
<td>4 Pt</td>
</tr>
<tr>
<td>Cathode Packing</td>
<td>NA</td>
<td>NA</td>
<td>5 Pt</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>4 Pt</td>
<td>4 Pt</td>
<td>4 Pt</td>
</tr>
<tr>
<td>electrode total A/C</td>
<td>1/1</td>
<td>2/1</td>
<td>½</td>
<td>1/1</td>
<td>1/1</td>
<td>2/1</td>
<td>2/2</td>
<td>2/2</td>
<td>2/1</td>
<td>2/1</td>
<td>2/1</td>
</tr>
<tr>
<td>Electrode Material</td>
<td>Pt</td>
<td>Pt</td>
<td>Pt</td>
<td>Pt</td>
<td>Pt</td>
<td>Pt</td>
<td>Pt</td>
<td>Pt</td>
<td>Pt</td>
<td>Pt</td>
<td>Pt</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>Au</td>
<td>Au</td>
<td>Au</td>
<td>Au</td>
<td>Au</td>
<td>Au</td>
<td>Au</td>
<td>Au</td>
<td>Au</td>
<td>Si</td>
</tr>
<tr>
<td></td>
<td>316</td>
<td>316</td>
<td>316</td>
<td>316</td>
<td>316</td>
<td>316</td>
<td>316</td>
<td>316</td>
<td>316</td>
<td>316</td>
<td>316</td>
</tr>
</tbody>
</table>
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The economics presented within this thesis show reasonable evidence that it is beneficial to continue research on both low voltage hydrogen production techniques. It appears that H$_2$S electrolysis can be a more economical waste treatment process for power plants and refineries than the Claus process. It also appears that electrochemical sulfuric acid and hydrogen production is a viable alternative to typical sulfuric acid production.

It can be concluded that the initial problems with SO$_2$ diffusion have been alleviated. The flow gradient with liquid electrolyte seems to limit the diffusion of SO$_2$ with less harm to the overall resistance of the system than the addition of an intermediate chamber in the solid electrolyte cell. This seems logical because Nafion® has a much lower conductivity than sulfuric acid and two pieces are needed for the 3 compartment cell. The lower conductivity is typically over come by the thin sheets of membrane that are used and the intimate contact made between the electrode, catalyst and membrane when the MEAs are hot pressed.

There in lies part of the solution for better current density in the three compartment cell. First of all thinner membranes should be used. Other membranes with better conductivity should be looked into. Better MEA production processes should be developed or commercial MEAs purchased.

Just as catalyst deposition is an issue in MEA production it is also a major draw back to electrode production for the liquid electrolyte cells. It appears Pt has a good effect on the cathode which is beneficial because it will make a good Schottky barrier when the solar cells are developed.

The short comings happen at the anode. It appears that the corrosion problems at the anode have been overcome by electroplating gold.
Unfortunately gold does not appear to be catalytically active for sulfuric acid production. Extensive work needs to be done to develop an anode catalyst. This work as well as historical shows that RuO$_2$ is a candidate for the anode catalyst. The issues with RuO$_2$ loss after long term electrolysis needs to be further investigated and corrected. Historical data also suggests WC as a good anodic and cathodic catalyst candidate. Deposition techniques for WC need to be investigated.

The experiments manipulating the electrolyte bridge show that the original design minimizing the cross sectional area of the electrolyte bridge to inhibit SO$_2$ diffusion adversely affected the performance of the cell. They show that more design changes increasing the cross sectional area in the anode compartment and cathode compartment are needed to maximize the current density while still inhibiting SO$_2$ diffusion.

It also appears that is may be necessary to return to the usage of liquid SO$_2$ to increase the concentration of SO$_2$ in the anode compartment. The last experiments with two cathodes and ¼” anode compartment and one cathode and ½” anode compartment show greater current, at 1.1 and 1.2 volts, than can be maintained at the flow rate and concentration of SO$_2$ used in these experiments. This is possible at the short times due to residual SO$_2$ not reacted at lower voltages and currents. Increasing the flow rate can increase the amount of SO$_2$ but is does not appear to show a large improvement in current according experiments not reported in this thesis. This suggests the need for increased concentration is preferable to increased flow rate. The concentration can be increase in the SO$_2$ saturated H$_2$SO$_4$ by increasing pressure, but it would be much easier to introduce liquid SO$_2$. 
REFERENCES


APPENDICES
Appendix A: Data Acquisition Hardware and Programs

Figure A.1 Power Supply Control Labview User Interface
Appendix A: (Continued)

Figure A.2 Power Supply Control Labview Block Diagram

Figure A.3 Data Acquisition Control Labview User Interface
Appendix A: (Continued)

Figure A.4 Data Acquisition Control Labview Block Diagram
Appendix B: Characterization Equipment

Following are pictures and specifications of the characterization equipment used in the thesis. They can be found on the website for the University of South Florida Nanomaterials and Nanomanufacturing Research Center, http://nnrc.eng.usf.edu/Labs&Resources/toollist.asp?id=2.

Figure B.1 Hitachi S-800 Scanning Electron Microscope

<table>
<thead>
<tr>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 nm Resolution</td>
</tr>
<tr>
<td>300,000X mag.</td>
</tr>
<tr>
<td>Cold cathode field emission source</td>
</tr>
<tr>
<td>Accepts specimens up to 25 mm dia., by 20 mm height</td>
</tr>
<tr>
<td>EDAX-Phoenix EDS System</td>
</tr>
</tbody>
</table>

Figure B.2 Hitachi S-800 Specifications
Appendix B: (Continued)

Figure B.3  X'Pert Diffractometer

<table>
<thead>
<tr>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selectable line or point focus 1.8kW sealed ceramic copper x-ray tube source</td>
</tr>
<tr>
<td>Choice of PreFIX incident beam optics include:</td>
</tr>
<tr>
<td>For Line Focus Applications-</td>
</tr>
<tr>
<td>Fixed Divergence Slit Module</td>
</tr>
<tr>
<td>X-Ray Mirror with automatic attenuator</td>
</tr>
<tr>
<td>Hybrid 4-bounce Monochromator with automatic attenuator</td>
</tr>
<tr>
<td>For Point Focus Applications-</td>
</tr>
<tr>
<td>Ge [440] Monochromator</td>
</tr>
<tr>
<td>Crossed slits Collimator</td>
</tr>
<tr>
<td>Choice of PreFIX diffracted beam optics include:</td>
</tr>
<tr>
<td>Triple axis setup utilizes a three bounce (022) channel cut Ge crystal to provide an acceptance angle of 12 arc seconds</td>
</tr>
<tr>
<td>The parallel plate collimator with a Flat Crystal Monochromator</td>
</tr>
<tr>
<td>Programmable Receiving Slit with Fixed Anti scatter Slit and a curved crystal monochromator</td>
</tr>
<tr>
<td>High resolution goniometer with optically encoded sample positioning enables a minimum step size of 0.0001°</td>
</tr>
<tr>
<td>1/2 circle Eulerian cradle with motorized sample stage enables sample tilts of +/-90°, in-plane rotation of 360°, in-plane X and Y translations of 100 mm, and vertical Z displacement of 11 mm</td>
</tr>
<tr>
<td>2 sealed proportional detectors with a large dynamic range</td>
</tr>
</tbody>
</table>

Figure B.4  X'Pert Diffractometer Specifications
Appendix B: (Continued)

Figure B.5 Anatech Limited Hummer X Sputter Coater

<table>
<thead>
<tr>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max Current: 20 mA</td>
</tr>
<tr>
<td>Max Voltage: 3000 V.D.C.</td>
</tr>
<tr>
<td>Modes: Plate, Etch, Plasma</td>
</tr>
<tr>
<td>Base Vacuum: 20 mT</td>
</tr>
<tr>
<td>Target: 3 inch Gold Palladium</td>
</tr>
</tbody>
</table>

Figure B.6 Anatech Limited Hummer X Sputter Coater Specifications
Appendix B: (Control)

Figure B.7 Plasma Sciences CRC-100 Sputter Tool

<table>
<thead>
<tr>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power supplies: DC- 150watts max, RF 200watts</td>
</tr>
<tr>
<td>Target: 2” diameter fixed x .125” thick maximum</td>
</tr>
<tr>
<td>Sample size: up to a 4” wafer</td>
</tr>
<tr>
<td>Target to sample distance: 2”- 4” adjustable</td>
</tr>
<tr>
<td>Vacuum system: Welsh duo roughing pump Alcatel 5081 turbo pump, 15min pumpdown time.</td>
</tr>
<tr>
<td>Cooling water: .5 lpm</td>
</tr>
<tr>
<td>Gases: Argon</td>
</tr>
<tr>
<td>Power: 120Vac 15amps</td>
</tr>
</tbody>
</table>

Figure B.8 Plasma Sciences CRC-100 Sputter Tool Specifications

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Appendix C: Cell Drawings

Following are two dimensional drawings of the individual sections of the low pressure two inch cell.

Figure C.1 Low Pressure Cell Anode Compartment
Appendix C: (Continued)

Figure C.2 Low Pressure Cell Electrode Assembly

Figure C.3 Low Pressure Cell Cathode Compartment
Appendix C: (Continued)

Following are two dimensional drawings of the individual sections of the 80 psig two inch cell.

**Figure C.4 80 psig Cell Anode Compartment**
Appendix C: (Continued)

Figure C.5 80 psig Cell Electrode Assembly
Appendix C: (Continued)

Figure C.6 80 psig Cell Cathode Compartment