ASSESSMENT OF COAL AND GRAPHITE ELECTROLYSIS

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This thesis entitled

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Electroplated carbon fiber electrodes with noble metals (Pt, Rh, Pt-Rh, Pt-Ir, and Pt-Ir-Rh) are evaluated on a sandwich configuration coal electrolytic cell (CEC) for the electrolysis of coal and graphite under galvanostatic conditions. Among Pt, Rh, Pt-Rh, Pt-Ir, and Pt-Ir-Rh electrodes with the same loading (5 mg/cm of fiber), Pt and Pt-Ir seem to produce the highest CO$_2$ faradic efficiency. Factorial design is used to determine the effect of loading and composition on the electrooxidation of coal and graphite to CO$_2$. The effect of abrasion on the coating of the electrodes is determined by performing weight change analyses. Pt and Pt-Rh electrodes are significantly affected by erosion (above 10% weight loss). The presence of graphite has a positive effect on the electrooxidation of coal to CO$_2$ in a graphite-coal slurry mixture. The energy consumption for the production of hydrogen from the electrolysis of coal is about 22 Wh/g of H$_2$ for all the electrodes tested (50 % lower than that for hydrogen production by electrolysis of water under similar operating conditions). This fact shows that coal electrolysis is a competitive method for in situ hydrogen generation.
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CHAPTER 1: INTRODUCTION

1.1 Project Overview

Diminishing resources of fossil fuels such as petroleum and natural gas have made researchers look for an alternative for fuel which is much cleaner, abundant and cheaper than currently used options. Hydrogen can be looked at as a promising option in this regard because it is clean and abundantly available in nature in various compounds.

Among many sources from which hydrogen can be obtained, coal is a very attractive option, due to its low cost and large supply. However, a traditional method such as coal gasification has some disadvantages, such as very high operating temperature (around 800°C) and pressure (1 to 100 atm) [1], evolution of harmful pollutants such as SO\textsubscript{x} and NO\textsubscript{x}, need of separation and purification of gaseous products, etc. All these disadvantages are overcome by electrolysis of coal slurry [1] which can produce hydrogen on site as per demand and has lower theoretical voltage than that of water electrolysis.

However, the mechanism of this process is not fully understood. Hence, it is imperative to get an insight into various factors such as: electrode composition, effect of additional contents such as iron present in coal compared to pure carbon on the current densities. Hence, the present study compares the reactivity of coal and graphite on different electrode materials. Graphite was chosen because it is one of the pure forms of carbon and its study would help understand the role of surface structure.

This research is significant because it will provide a better understanding of a new technology that can allow processing coal in an environmentally friendly manner.
1.2 Significance of Research

Coal has been used for the production of hydrogen for many years. The process of converting coal into gaseous products is known as gasification of coal. However, the traditional methods have many disadvantages as described in the earlier section. In 1979, Coughlin and Farooque [1] came up with a new method for H\textsubscript{2} generation from coal via electrolysis. Coal slurry when subjected to an electric current gives two distinct products at the two electrodes.

At anode, oxidation of coal slurry gives CO\textsubscript{2} according to the following reaction:

\[ C_\text{(s)} + 2H_2O_{(l)} \rightarrow CO_2(g) + 4H^+ + 4e^- \quad (1) \]

And at the cathode, reduction product is H\textsubscript{2} as follows:

\[ 4H^+ + 4e^- \rightarrow 2H_2(g) \quad (2) \]

The sum of the reactions (1) and (2) gives the overall reaction for electrochemical gasification of coal:

\[ C_\text{(s)} + 2H_2O_{(l)} \rightarrow 2H_2(g) + CO_2(g) \quad (3) \]

In coal gasification, sulfur appears in the product stream in the form of SO\textsubscript{x}. However, the electrochemical oxidation of sulfur takes place at -0.451 V as shown below.

\[ S_\text{(s)} + 2H_2O \rightarrow SO_2(g) + 4e^- + 4H^+ \quad E^\circ = -0.451 \text{ V} \quad (4) \]

From the above equation it can be observed that the potential that needs to be provided for equation (4) is higher than that required for the electrolysis of coal slurry (0.21 V) [1]. Hence, oxidation of sulfur in coal to sulfur oxides is not favorable from a thermodynamic point of view.
This process produces relatively pure streams of carbon oxides at the anode and H\textsubscript{2} at the cathode compared to the mixture of H\textsubscript{2}, CO, CO\textsubscript{2} and other impurities produced in the conventional gasification method. H\textsubscript{2} can be directly fed to a fuel cell for energy generation.

Electrochemical gasification of coal slurry to generate H\textsubscript{2} is thermodynamically more favorable than water electrolysis for production of H\textsubscript{2}. Electrochemical gasification requires only 0.21 V of theoretical driving potential as compared to water electrolysis which takes place at theoretical potential of 1.23 V [1].

The main research challenge in this regard is that even if the process looks very attractive from a thermodynamic point of view, it is not kinetically favorable. This challenge can be overcome by developing a better cell design and electrodes with high surface areas.

The U.S. Department of Energy has the goal to produce H\textsubscript{2} at $2.00/Kg. H\textsubscript{2} production via electrolysis of coal slurry will cost $ 0.89/kg for the production capacity of 470 kg/day (for forecourt production pathway) based on thermodynamic calculations. The proposed research at the EERL (Electrochemical Engineering Research Laboratory) surely satisfies the standards set by the Department of Energy but also assures green way of producing H\textsubscript{2}.

1.3 Statement of Objectives

Hydrogen can be looked at as an attractive option as a fuel for the future use. It is clean and abundantly available in nature. Depleting reserves of oil and gas make the use of hydrogen even more important.
Coal has been used for generation of hydrogen for many years. It is cheap and plentiful. However, the traditional method of coal gasification has certain shortcomings. This process is operated at a very high temperature, generally around 800ºC. Gasification products have to be cleaned, separated, and purified. It is not environmentally friendly because it produces harmful gases such as SO\textsubscript{x} and NO\textsubscript{x}. On the other hand, hydrogen generation via electrolysis of coal slurry is a very clean process. It operates at low temperatures, 40-80ºC. Two pure streams of gases, namely hydrogen and carbon dioxide are obtained at cathode and anode respectively. Additionally, this process can produce hydrogen on site to suit the demand.

The EERL at Ohio University is working to develop competitive technologies for the production of H\textsubscript{2} from different sources such as coal, ethanol and ammonia. One of the long term research goals of this laboratory is in-situ hydrogen generation using electrolysis of coal slurry rather than by a traditional method such as coal gasification. In 1979, Coughlin and Farooque [1] provided some fundamental understanding of this process, but very little research has been conducted in this area until now.

The main challenge is to improve the kinetics of this process. Low currents obtained by previous researchers [1, 2, 5, 7] can be attributed to mainly two facts.

1. The electrodes used by these researchers were in foil forms. EERL has recently developed [15] novel carbon fiber electrodes by plating noble metals on the carbon fibers. This technology would make it possible to improve the surface area of the electrodes, thus yielding higher currents.

2. The cell design used by these researches offered high resistance to
electrooxidation of coal and yielded low currents. It is our hypothesis that a better design for the electrolytic cell would decrease the ohmic resistance of the system and thus lead to obtaining higher currents.

Additionally, graphite can be used as a baseline to compare the electrooxidation of coal and graphite slurries and study the effect of surface structure. This study will help to understand whether surface structure of coal plays an important role in the efficiency of the process.
CHAPTER 2: LITERATURE REVIEW

Coughlin and Farooque [1] were the first to bring forth the electrochemical gasification of coal. According to thermodynamic principles, electrolysis of coal slurry requires only 9.5 kcal of electrical energy per mole of $\text{H}_2$ as compared to 56.7 kcal per mole of electrical energy for electrolysis of water. The authors [1] also found that there should be a contact between anode and coal because when the anode was isolated by a porous membrane from coal, very low currents were observed. They estimated the activation energy for North Dakota Lignite at 1 V to be 10-12 kcal/mol.

In the galvanostatic studies involving electrolysis of North Dakota Lignite, the authors [1] found that as the reaction proceeds, coal becomes unreactive and the potential rises to keep the reaction rate constant. After initial oxidation at 150 mA until 9.82 % of coal was consumed, the electrooxidation was carried out at a lower current of 100 mA. Within the first span of electrooxidation (at 150 mA), the potential gradually rose to about 1.2 V and then showed a sudden jump to 1.7 V. This behavior was reproducible when the experiment was repeated at 100 mA.

Coughlin and Farooque [2] also studied the effect of operating parameters on the electrooxidation of coal slurry. They investigated the effect of particle size, coal concentration and temperature. The researchers also reported the studies about activation energy and the course of electrochemical gasification reaction. They found that the larger the particle, the greater is the probability of it to strike the anode. In addition, the smaller the particle, the greater surface area it has and thus should give more reaction per unit mass basis. When the authors studied the three particle size ranges (210-250 $\mu$m, 105-125
µm, less than 44 µm) of North Dakota Lignite they found out that for the course of long-
term electrooxidation of coal the smaller particles provided higher rates. The effect of 
coal concentration was found to be large at smaller concentrations. The authors also 
found that the rate of oxidation falls as the reaction proceeds and the reversible 
thermodynamic potential decreases with increase in temperature. They also investigated 
the electrolysis of graphite [2]. Graphite was chosen, as it is one of the pure forms of 
carbon. The oxidation currents observed for the graphite were an order of magnitude 
lower than that of coal.

Coughlin and Farooque [3] discussed different alternatives for the electrode and 
electrolyte for the electrooxidation of coal slurry. Graphite anode when subjected to 
experimental conditions showed very small (always less than 0.01 mA) oxidation 
currents in the absence of coal. These values were less as compared to when coal was 
present in the slurry. The authors also tested different electrolytes such as H₃PO₄, 
trifluoromethane-sulphonic acid (TFMSA) along with H₂SO₄. It was found that H₃PO₄ 
showed much poorer performance than H₂SO₄. Oxidation currents for H₃PO₄ were about 
10 % of that for H₂SO₄ for Pittsburgh Coal under the same conditions. For similar 
conditions TFMSA exhibited comparable reaction rates to that for H₂SO₄. However, due 
to conductive superiority, H₂SO₄ was found to be the most favorable electrolyte.

Coughlin and Farooque [4] compared the energy efficiency of electrochemical 
coal gasification with different processes. According to them thermodynamic efficiency 
for electrochemical coal gasification is smaller by about 50 % than the conventional coal 
gasification process at potentials of about 1 V. This efficiency is known to be much
favorable at low operating potentials or higher temperature operation. They [4] further stated that coal concentration, temperature and electrode surface area are some of the key parameters which can lower the volume of the reactor. The authors did not observe any sulfur compounds and loss in $\text{H}_2\text{SO}_4$ quantity during the course of the experiments.

Okada et al. [5] tested slurries of anthracite and lignite in 4.15 M $\text{H}_2\text{SO}_4$. They also found that evolution of hydrogen at cell potentials occurred at voltages more negative than 0.6 V. The limiting current density (5-10 mA/cm$^2$) remained almost the same when experiments were carried out on solution remaining after the coal was filtered off. However, when coal was washed, the limiting current density for hydrogen evolution at low potential reduced to 0.1 mA/cm$^2$. The authors found higher CO$_2$ efficiency in the case of carbon than in the case of coal. This observation was found to be in agreement with the results presented in this study related to the electrooxidation of coal and graphite on noble carbon fiber electrodes. The discussion of these results is presented in Chapter 3. The authors further argued that coal has many impurities which get dissolved during the formation of slurry. These species also undergo oxidation reactions which lead to formation of compounds other than CO$_2$. Besides, coal has carboxyl, nitrogen and sulfur containing terminal molecules which may act as reactive centers giving rise to other products. This argument is supported by the fact that lignite which has more terminal groups gives higher currents. The authors further found that in the presence of Fe$^{2+}$ originating from coal, the current densities were 5-10 mA/cm$^2$ at a cell potential of 0.8 V, 80 °C, 4.15 M $\text{H}_2\text{SO}_4$ concentration. In the absence of Fe$^{2+}$, the evolution rate of $\text{H}_2$ reduced to an impractical order of 0.1 mA/cm$^2$. They [5] reported two types of anodic
reactions-first, which involves direct collision of slurry particles with the electrode, where as the second type of reaction occurs in the presence of coal and involves the partial anodic oxidation of products dissolved there from.

Baldwin et al. [6] investigated the voltammetric and electrolytic behavior of different coals in aqueous and organic solvents. For aqueous coal slurries, anodic currents started at +0.4 V versus Standard Calomel Electrode (SCE). However, in the case of organic solvents like acetonitrile and dimethylsulfoxide this phenomenon occurred at more positive potentials than that for aqueous solvents. The authors stated that aqueous coal extract contains iron and oxidation of Fe$^{2+}$ to Fe$^{3+}$ is mainly responsible for the anodic currents and hence the electrochemical activity of coal slurries is expected to be largely dependent on the solvent selected. Potentiostatic studies showed that approximately 1V of potential difference yielded the onset of oxidation currents. These currents were again attributed to the oxidation of Fe$^{2+}$ which leached out from coal.

Dhooge et al. [7] proposed that the iron ions leached out from coal are responsible for major anodic current. According to them Fe$^{2+}$ is electrolytically oxidized to Fe$^{3+}$ at the anode, which in turn oxidizes coal. Coal has been represented by carbon in the reaction, because oxidation of carbon in coal is important in this regard.

\[
4Fe^{3+} + C + 2H_2O \rightarrow CO_2 + 4Fe^{2+} + 4H^+ \quad (5)
\]

This is followed by reoxidation of Fe$^{2+}$ to Fe$^{3+}$ at the anode. This is feasible thermodynamically because the standard electrode potential (Eº) for Fe$^{3+}$/Fe$^{2+}$ is at least 0.5 V higher than that of the carbon oxidation to CO$_2$.

Similar reaction can take place for cerium as follows:
\[4Ce^{4+} + C + 2H_2O \rightarrow CO_2 + 4Ce^{3+} + 4H^+\]  \hspace{1cm} (6)

And reoxidation of Ce\(^{3+}\) to Ce\(^{4+}\) as:

\[Ce^{3+} \rightarrow Ce^{4+} + e\]  \hspace{1cm} (7)

The authors observed that the current in the case of cerium was one order of magnitude more than that in the case of iron. However, to determine whether the above mentioned process is the only way for coal oxidation, authors ran experiments on coal as well as coal extracts for several (100) hours. They observed that the active species become completely exhausted after 15 hours in the coal extract, on the other hand, in coal slurry current decays slowly for the first 15 hours and then maintains steady level for more than 100 hours. This result is in agreement with that obtained by Coughlin and Farooque [2] and suggests that the oxidation of Fe\(^{2+}\) is not the only process that is occurring in the coal slurry oxidation. On the basis of experimental results, Dhooge et al. [7] proposed that reactions (5) and (6) are the rate limiting steps.

Coughlin and Farooque [8] suggested that energy efficiencies greater than 50 % can be obtained by carrying out the reaction at operating potentials lower than about 0.7 V. The partially consumed (11-30 %) solid residues were enriched in oxygen and depleted in hydrogen-rich volatile matter after the course of the reaction. The heating value of all the samples was decreased. In addition, the authors stated that depending on the mode of the reaction (potentiostatic or galvanostatic), the selectivity of the reaction for different components of the solid fuels was different. For North Dakota lignite the authors observed the following facts: hydrogen rich volatile matter was preferentially consumed, reacted portion of the carbonaceous solid was enriched in fixed carbon as a
result of electrochemical reaction, the decrease in sulfur and ash content might be attributed to reactions between acidic electrolyte and non carbonaceous coal minerals (like basic oxides and sulfides) which liberate $\text{H}_2\text{S}$ and dissolve metallic oxides. The increase in oxygen content was in agreement with their earlier hypothesis [1,2] that surface functional groups such as carboxyl, carbonyl and hydroxyl oxygen are reaction intermediates that accumulate on the solid reactant. The authors also tested Pittsburgh Seam coal. Similar results as those obtained for lignite were found. Galvanostatic tests gave similar trend in change in oxygen content and volatile matter. However, potentiostatic experiments gave very different results compared to lignite. It was observed that the ratio of volatile matter to fixed carbon ($V_m/FC$) in product increased. This fact suggests greater selectivity of potentiostatic reaction for $F_C$ (fixed carbon) than $V_m$ (volatile matter). Minnesota Red Sedge Peat was also tested. It was found that some fixed carbon but mostly volatile matter was consumed during the reaction. Far more carbon and hydrogen were removed than the corresponding equivalents of currents passed during the oxidation. This fact suggests that the unaccounted material dissolved or became dispersed as a sol in the electrolyte. In spite of the decrease in oxygen content, O/C ratio increased as a result of the anodic oxidation.

In addition, Dhooge and Park [9] stated that the overall reaction might be the sequence of one electron transfer reactions. Carbon oxides are first formed on the coal surface which is then followed by the final product formation ($\text{CO}_2$). The authors [9] also tested other catalyst oxidants like bromine and $\text{Ce}^{4+}$. These authors further argued that coal contains reactive sites which are oxidizable by $\text{Fe}^{3+}$ which may not exist in relatively
pure carbonaceous sources like graphite and hence could give the explanation of low currents for graphite. The authors found the reaction order of coal to be one which is same as that for a metal ion. This fact confirms another fact that one metal ion should not be able to react with more than one coal functionality in parallel. The authors described some characteristics for a redox couple as follows: should have as low standard electrode potential as possible and at the same time be able to oxidize coal at a faster rate, both species should be soluble in large extent in water or acid solution, should be stable over a long period of time, should have a relatively large heterogeneous electron transfer rate constant at the electrode, should be relatively inexpensive.

The authors [9] believed that not all metal ion reactions with coal produce CO$_2$; some of the reactions take place partially and do not lead to CO$_2$ immediately. Among many model compounds like p-benzoquinone, phenol, benzoic acid, mellitic acid, 1,4-naphthoquinone, 2-naphthol, 2-naphthoic acid, anthroquinone and 2-anthanoic acid tested by authors only p-benzoquinone exhibited significant CO$_2$ production rate. They further argued that low ranked coals react faster than high ranked coals due to more number of reactive sites.

Taylor et al. [10] studied the anodic oxidation of slurries of lignite, bituminous, and anthracite coals, a high yield extract of coal and carbon black. The authors found that the rate of CO$_2$ evolution by an attack by an acidic electrolyte before passage of current was dependent on ash content of the coal. Voltametric and mass spectroscopic experiments revealed that there are two kinds of anodic activities below 1.6 V across the cell. Near 1-1.2 V, the electrochemical activity mainly arises from the conversion of
leached Fe$^{2+}$ to Fe$^{3+}$. Further activity near 1.4-1.5 V can be attributed to the oxidation of leached organic matter to CO$_2$. In addition, both kinds of activities can be suppressed by prolonged washing of the coal with electrolyte and are present in the filtrate from the slurries. The authors [10] further investigated that the magnitude of both currents depend markedly on coal rank, with a lignite showing greater activity than two bituminous coals and an anthracite only small activity. A supercritical gas extract from coal showed no anodic activity below 1.6 V. In addition, the authors stated that the inorganic ions leached from coal do not play an important role in oxidation to gaseous products. Their main influence was to reduce the fraction of the current leading to gas evolution. They further stated that electrochemically generated ferric ions may slowly oxidize coal to gaseous products, but at typical concentrations found in coal slurries this process is negligible.

Murphy and Bockris [11] tested lignite washed with water and also the filtrate of the slurry by using Sep-pak cartridges. They concluded that the current was influenced by pH, electrocatalyst, abrasion of coal particles, and intermediate redox reactions.

Lalvani et al. [12] electrolyzed Illinois No. 6 coal at mild conditions to remove sulfur and ash. The process involves oxidation of organic sulfur and pyrite in coal to water soluble forms. The authors used acidic as well as basic mediums for their experiments. They electrolyzed coal in 9 % HCl at a potential of 1.4 V vs. SCE. They observed high currents at the beginning of electrolysis due to oxidation of mineral matter like FeS$_2$. However, as the reaction progressed the rates of the reaction declined and assumed limiting values due to dominance of oxidation of less reactive carbonaceous material in that phase. This hypothesis is in agreement with the explanation by the other
authors [2, 4, 5]. This experiment resulted in 48 % of sulfur removal and 54 % of ash removal. The authors also tried to electrolyze the coal slurry in basic medium with NaOH as an electrolyte. Electrolysis at 1.4 V vs. SCE achieved 27 % sulfur while an increase in the electrode potential to 3 V vs. SCE achieved 40 % sulfur removal. Electrolysis at low potentials (1.4 V vs. SCE) resulted in an increase in ash content of coal. The authors proposed that OH\(^-\) undergoes charge transfer at the anode to produce highly reactive OH radicals which in turn attack organic sulfur and oxidize it to water soluble sulfones and sulfates.

Nand et al. [13] studied the properties and reactivities of solid residue from coal electrolysis. The authors found an onset of evolution of volatile matter around 400°C. It peaked sharply at 500°C and dropped off very rapidly above 500°C. They stated that for most coals the pyrolytic reactions occur between 400°C and 600°C. The rate of weight loss became constant at 700°C and remained approximately at the same level up to 800°C. The authors also reported that pyrolysis between 700°C and 800°C was accompanied by secondary reactions of char and released gases. However, acidic electrolysis led to a rapid weight loss at as low as 250°C. The two weight loss maxima were found at 300°C and 500°C. The maximum observed at 550°C for an unreacted coal became less pronounced after electrolysis. When the anodic potential and hence the rate of electrochemical reaction was increased, the maximum pyrolysis weight loss at 300°C as mentioned above became more pronounced. When electrolysis was carried out in basic medium (NaOH) some increase in pyrolysis weight loss in the range of 150-400°C was
found to be increased. The authors found that as compared to raw coal, electrolysis rendered coal more soluble in a mixture of benzene and ethanol.

Recently, Patil et al. [14] investigated the electrooxidation of coal slurries on different electrode materials. The authors reported that Pt-Ir seems to be a good electrode for the electrolysis of coal. Furthermore, they reported the positive synergistic effect of the presence of Fe$^{+2}$ and Fe$^{+3}$ on the electrolysis of coal. Current densities as high as 30 mA/cm$^2$ were reported due to the synergistic effect of these cations on the electrolysis of coal during potentiostatic operations. However, all the experiments were performed in batch cells with single compartments.

While summarizing the work of previous researchers, it was found that the main challenges in the process of electrolyzing coal slurry are to improve the sluggish kinetics and determine the role of surface structure of coal in the efficiency of the process. The objectives of the present study focus on the same issues to find possible solutions to the above mentioned problems.
CHAPTER 3: ASSESSMENT OF COAL AND GRAPHITE ELECTROLYSIS ON CARBON FIBER ELECTRODES

It should be noted that this chapter appears as a manuscript which has been submitted to the Journal of Power Sources for consideration for publication by Nilesh Sathe and Gerardine Botte.

3.1 Research Objectives

All the results reported in the open literature on the electrolysis of coal have been performed in batch glass cells. Typical cells used consisted of a glass vessel with outlets for gas collection, and electrodes made of noble metal foils [1]. The cathode compartment was separated from the anode by fritted glass [1]. Other authors had used cells where the anode and cathode compartments were separated by a saturated K$_2$SO$_4$ salt bridge [7]. It is hypothesized that a better design of the coal electrolytic cell will decrease the ohmic resistance and higher currents could be observed. Within this context, the objectives of this paper focus on the improvement of the electrooxidation rate of coal. This paper has three objectives:

1. Evaluate the performance of noble metals deposited on carbon fibers substrates (nobel-carbon fibers electrodes) on the electrooxidation of coal. Recently, the Electrochemical Engineering Research Laboratory (EERL) at Ohio University has developed novel electrodes for the electrolysis of different solid fuels [15] using carbon fibers as a substrate. The carbon fibers provide a large surface area for the electrooxidation reactions. Significant improvement of the current densities has been observed. According to Patil et al. [14], Pt-Ir performed better (it provided the highest
current density at a given cell voltage) than the other electrodes tested (Pt, Pt-Ru, and Pt-Rh). Botte [15] reported that Rh played a useful role to improve the electronic conductivity of the carbon fibers to facilitate plating and adherence of other noble metals. Because of the findings reported by Patil et al. [14] and Botte [15], the following noble metals were deposited on carbon fibers: Pt-Ir-Rh, Pt, Pt-Ir, Rh, and Pt-Rh. These electrode materials were tested in coal slurries to determine the best electrode material (based on CO\textsubscript{2} Faradaic efficiency) among them.

2. Determine the effect of catalyst loading on the electrooxidation of coal. In this paper, factorial design was used to perform a systematic study on the effect of catalyst loading and noble-carbon fiber electrode composition on the electrolysis of coal. This method makes sure that the interaction factors are also taken into account.

3. Compare the electrochemical performance of graphite with that of coal for all the electrodes mentioned in 3.1.1 and 3.1.2 to test out whether the surface structure of them plays an important role in the difference between their electrochemical activities. This difference was measured by calculating CO\textsubscript{2} Faradaic efficiencies.

Polarization techniques were used to achieve the objectives. All the experiments were performed in a continuous coal electrolytic cell sandwich configuration designed to minimize the ohmic resistance of the system.

3.2 Experimental Design

This study utilizes galvanostatic experiments to accomplish the proposed objectives. A description of the experimental design is given below.
3.2.1 Experimental Matrix

The most common method of designing experiments is varying one factor at a time and keeping others constant. However, this type of study does not allow examining whether interactions among factors exist [16]. Since this study is considered as the first effort to determine the effect of Ir composition and loading on the electrooxidation of coal slurries, it would be of interest to verify whether such an interaction between loading and composition exists. Therefore, factorial design was used for the design of the experimental matrix. The factors tested in the factorial design were Ir composition and loading. Each factor had two levels, low and high. The experimental matrix of the factorial design is given in Table 1.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Electrode</th>
<th>Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>1</td>
<td>Pt-Rh(1.7)</td>
<td>Low</td>
</tr>
<tr>
<td>2</td>
<td>Pt-Ir-Rh(1.7)</td>
<td>Low</td>
</tr>
<tr>
<td>3</td>
<td>Pt-Rh(9.9)</td>
<td>High</td>
</tr>
<tr>
<td>4</td>
<td>Pt-Ir-Rh(9.9)</td>
<td>High</td>
</tr>
</tbody>
</table>

Factor A represents loading (in mg of noble metal/cm of carbon fiber) and has two values, 1.7 and 9.9 representing low and high levels, respectively. Factor B represents % Ir present in total Pt-Ir mass on the carbon fibers. Pt-Ir mass was 70 % by weight of total Pt-Ir-Rh mass. The low value for factor B was 0 % Ir by weight.
It was also necessary to identify the best noble-carbon fiber electrode for the electrooxidation of coal slurry to CO\textsubscript{2}. Patil et al. [14] reported that Pt-Ir was the best electrode for the electrooxidation of coal slurries. However, these electrode materials were used in the form of foils (metal alloys). Additionally, their conclusion [14] was based on the current density generated on the cell at a given voltage and they did not consider the Faradaic CO\textsubscript{2} efficiency. It was a major interest to determine whether Pt-Ir performed better than all the other electrode materials (in terms of the Faradic CO\textsubscript{2} efficiency) even in the plated form on the carbon fibers. The experimental matrix which was used to verify this fact is shown in Table 2.

**Table 2. Experimental matrix which comprises the different electrodes tested: Rh, Pt-Rh, Pt, Pt-Ir and Pt-Ir-Rh with the same loading of 5 mg/cm of carbon fiber**

<table>
<thead>
<tr>
<th>No.</th>
<th>Electrode</th>
<th>Loading (mg/cm of fiber)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh</td>
<td>5.0</td>
</tr>
<tr>
<td>2</td>
<td>Pt-Rh</td>
<td>5.2</td>
</tr>
<tr>
<td>3</td>
<td>Pt</td>
<td>5.1</td>
</tr>
<tr>
<td>4</td>
<td>Pt-Ir</td>
<td>5.3</td>
</tr>
<tr>
<td>5</td>
<td>Pt-Ir-Rh</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Table 2 gives the information about the electrodes tested and their corresponding loading. The electrodes tested were Rh, Pt-Rh, Pt, Pt-Ir, and Pt-Ir-Rh (all of them with a loading of 5 mg/cm of carbon fiber). The electrodes in which Rh is one of the constituents (Pt-Rh, Pt-Ir-Rh) have 30% by weight of total loading of Rh.
3.2.2 Preparation of Electrodes

The base support of the electrode was made up of 2x2 cm, 18 mesh titanium gauze woven of 0.28 mm diameter wire (open area 64.3% with a purity of 100 %) which was obtained from Alfa Aesar. The gauze served as a current collector for the carbon fibers and it was connected with a titanium wire (0.81 mm OD, 15 cm long with a purity of 99.7 % on metals basis) by making sure that the resistance across the joint is low (0.2-0.3 Ω). Titanium was chosen to stand the corrosive acidic media at the operating temperature. Polyacrylonitrile (PAN) based carbon fibers (Celion G30-500, 7µm diameter) were obtained from BASF and were used for the substrate of the electrodes. The carbon fibers were wound on the titanium gauze. Typically 34 cm long bundles of fibers (with approximately 6000 fibers per bundle) were used to ensure a uniform coverage of titanium gauze. After winding on the gauze, the ends of these fibers were combined together and then tighten on the stem of the electrode. These were then fixed to the stem with the help of a small titanium clip. Figure 1 shows a schematic diagram of the procedure that was used for the fabrication of the electrodes. The electrodes were cleaned with acetone to remove greasy compounds and they were weighed before and after plating.

Plating salts of 99.9 % purity were obtained from Alfa Aesar. Dihydrogen hexachloroplatinate (IV) (Pt: 38 %), Rhodium (III) chloride (Rh: 38.5 %), and Iridium (III) chloride (Ir: 55 %) were used to plate Pt, Rh, and Ir, respectively. The order of plating is summarized in Table 3. For making Pt electrodes the electrodes earlier wound with carbon fibers were directly plated in a Pt solution bath.
3. Wrap the Carbon Fibers around the Gauze.

Titanium Gauze Electrode: 18 mesh woven from 0.28 mm dia. Wire. Open Area 64.3%, 100% Purity

Titanium Wire: 0.81 mm dia. 99.7% Purity Annealed

PAN-based Carbon Fibers (Celion G30-500, 7 μm dia. 6000 Filaments per Bundle)

20 cm approx.

Carbon Fiber Ready for Electro-deposition Procedure

1. Clean with Acetone
2. Measure Weight
3. Wrap the Carbon Fibers around the Gauze.
4. Clean with Acetone
5. Dry with air
6. Measure Weight

For Pt-Ir, Pt and Ir were plated simultaneously. All the other electrodes which contain Rh were first plated with Rh (first layer) in a Rh salt solution bath. Rh was used to improve the electronic conductivity of carbon fibers making the plating of other noble

Figure 1: Schematic representation of the procedure used for the preparation of the carbon fiber electrodes (originally drawn by Elizabeth Cellar, undergraduate research student at the EERL Ohio University).
Table 3. Order of plating of different noble metals on carbon fibers

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Order of plating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>Pt</td>
</tr>
<tr>
<td>Rh</td>
<td>Rh</td>
</tr>
<tr>
<td>Pt-Rh</td>
<td>First layer Rh</td>
</tr>
<tr>
<td></td>
<td>Second layer Pt</td>
</tr>
<tr>
<td>Pt-Ir-Rh</td>
<td>First layer Rh</td>
</tr>
<tr>
<td></td>
<td>Second layer Pt-Ir (co-deposited)</td>
</tr>
<tr>
<td>Pt-Ir</td>
<td>One layer, Pt-Ir were co-deposited</td>
</tr>
</tbody>
</table>

metals easier as reported by Botte [14]. After plating with Rh, the other noble metals were plated in their respective plating baths.

Table 4 summarizes the conditions of the plating procedure for Pt, Rh, and Pt-Ir. The corresponding procedure was adjusted and repeated accordingly so as to prepare the electrodes discussed in Tables 1 and 2. The plating procedure for Pt is explained as an example. The plating solution was prepared by dissolving the appropriate amount of $\text{H}_2\text{PtCl}_6$ (to achieve a concentration of 0.8 mg/ml, Table 4) in 1M HCl prepared using ultra high purity water. The solution was heated to 80°C and stirred with a stirring bar. The counter electrode was made up of Pt foil. The process of electrodeposition of Pt was carried out galvanostatically at 100 mA in intervals of 20-30 minutes (Table 4). An ARBIN cycler BT2000 was used to control the current.
Table 4. Important experimental parameters for plating of Rh, Pt, and Pt-Ir on the carbon fibers

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Rh</th>
<th>Pt</th>
<th>Pt-Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt</td>
<td>RhCl(_3)</td>
<td>H(_2)PtCl(_6)</td>
<td>H(_2)PtCl(_6) + IrCl(_3)</td>
</tr>
<tr>
<td>Concentration of salt (mg/ml)</td>
<td>0.5</td>
<td>0.8</td>
<td>0.4, 1.04</td>
</tr>
<tr>
<td>Temperature of plating bath (°C)</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Current (mA)</td>
<td>100</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td>Voltage range (V)</td>
<td>-1.2 to -1.3</td>
<td>-1.1 to -1.2</td>
<td>-0.8 to -1.3</td>
</tr>
</tbody>
</table>

During the process, it was ensured that the voltage range remained between -1.1 to -1.2 V to avoid the formation of Pt black. The total plating time was adjusted to obtain the different loading as explained in the experimental design (Table 1). Intermittently, after every plating interval the weight of the electrode was recorded to make sure the progress of plating was as desired. The above procedure was repeated for plating of other noble metals by suitably choosing appropriate parameters like plating salt, chemicals, concentration of plating solution, temperature, current, voltage range, and plating time as given in Table 4.

The electrodes were characterized by using a scanning electron microscope (SEM and EDX JEOL-2300), to ensure the quality of plating. Figure 2 shows the SEM of Rh with loading of 5.2 mg/cm of carbon fiber. It can be seen that the morphology of plating is flat. Rh seems to have good adherence properties since it forms continuous coating on the carbon fibers. During the plating all the fibers were covered uniformly.
Figure 3 shows the SEM of Pt with loading of 5.1 mg/cm of carbon fiber. It can be seen that the morphology of coating of Pt is different than that of Rh. Plating of Pt gives rise to sharp granules or dots as compared to flat coating in the case of Rh. However, all the carbon fibers were completely and uniformly covered.

![Plating of Rh](image)

Figure 2. SEM image of Rh with loading of 5.2 mg/cm of carbon fiber before testing at 750X

Figure 4 shows SEM of Pt-Ir-Rh with loading of 1.7 mg/cm of carbon fiber. Due to low loading the coverage of coating on the fibers was not good. Because of this, some fibers were only covered with the first layer of Rh. Some dots representing Pt-Ir can be seen, but they are not uniformly distributed due to low loading of the electrode. As loading increased (Pt-Ir-Rh with 5.1 mg/cm of carbon fiber, Figure 5) more fibers were coated. Also, the density of Pt-Ir dots increased.
Figure 3. SEM image of Pt with loading of 5.1 mg/cm of carbon fiber before testing at 750X

Figure 4. SEM image of Pt-Ir-Rh with loading of 1.7 mg/cm of carbon fiber before testing at 750X
Figure 5. SEM image of Pt-Ir-Rh with loading of 5.1 mg/cm of carbon fiber before testing at 750X

At high loading, 9.9 mg/cm of carbon fiber, Pt-Ir-Rh (Figure 6) shows increasing trend in the density of dots and the coverage of fibers. In this case only a small fraction of fibers was uncovered.

Figures 7, 8, and 9 represent Pt-Rh at low (1.7 mg/cm of carbon fiber), medium (5.2 mg/cm of carbon fiber), and high (9.9 mg/cm of carbon fiber) loadings, respectively. Similar observation in terms of coatings can be made as in the case of Figures 4, 5 and 6 respectively. However, in the case of medium loading of Pt-Rh, an unusual morphology of Pt was observed. However, this may be attributed to the fact that this SEM was taken near the edge of the electrode where high concentration of catalysts might have given rise to such an unusual pattern.
Figure 6. SEM image of Pt-Ir-Rh with loading of 9.9 mg/cm of carbon fiber before testing at 750X

Figure 7. SEM image of Pt-Rh with loading of 1.7 mg/cm of carbon fiber before testing at 750X
Figure 8. SEM image of Pt-Rh with loading of 5.2 mg/cm of carbon fiber before testing at 750X

Figure 9. SEM image of Pt-Rh with loading of 9.9 mg/cm of carbon fiber before testing at 750X
3.2.3 Construction of Coal Electrolytic Cell

A sandwich configuration was used for the coal electrolytic cell (CEC). Main constituents of the sandwich configuration are: polycarbonate plates, Teflon gaskets, membrane, and carbon fiber electrodes as shown in Figure 10.

![Figure 10: Schematic representation of the coal electrolytic cell (CEC)](image)

Polycarbonate plates (80x80 mm, 10 mm thick) and virgin electric grade Teflon gaskets (3.2 and 1.6 mm thick) were obtained from McMaster- Carr. A proprietary polyethylene membrane was used as separator and was obtained from a commercial manufacturer. The electrolytic cell was made of a sandwich configuration with two polycarbonate plates holding the electrode and membrane assembly between them. Holes
were made into the polycarbonate plates to facilitate the flow of slurry over the electrodes. The hoses (Precision Tygon® Lab, R-3603 Tubing) carrying the reactants (Figure 11) were fed into and out of the cell via these holes. The sealing of the cell was reinforced by attaching the Teflon gaskets (3.2 mm thick) with the help of silicon glue (GE Silicone I). A groove was made on the gaskets just to accommodate the thickness of the stem of the electrodes so that there was no gap present between the gasket and the plate when the electrodes were introduced. The cathode was placed on the gasket such that its boundaries lay within the area created by the holes. This ensured the uniform distribution of electrolyte over the electrode surface. The cathode of the cell consisted of Pt on carbon fibers with a loading of 9.1 mg/cm (see Section 3.2.2 for a description of the procedure used). One more gasket (1.6 mm thick) was added to the previous gasket to allow enough void volume in the compartments of the cell. The membrane was then attached to the other side of the gasket with glue in such a manner that it covered the window portion cut out of the gasket. Another gasket (3.2 mm thick) with groove for accommodating the electrode stem was then placed on the membrane. The anode was placed in such a way that it lay well within the area covered by holes on the plate. This was followed by one more Teflon gasket (3.2 mm thick) and the second polycarbonate plate. The reason behind putting an extra gasket on the anode side was to provide an extra space for the flow of coal/graphite slurry over the electrode surface and prevent the accumulation of coal/graphite particles in the pockets formed between the membrane and gasket. The two polycarbonate plates were then screwed together with the help of four screws.
The advantages of the sandwich cell configuration described above include:

1) Low cell resistance, as electrodes were placed very close to each other and separated just by a membrane.

2) Regular flow pattern of the circulating slurry over the surface of the electrode. The titanium gauze used as current collector also served as a flow distributing channel for the coal slurry.

3.3 Experimental Conditions and Methodology

The polarization experiments were carried out in the CEC shown in Figure 10. Sulfuric acid was used as the electrolyte with a concentration of 1 M. Pittsburgh No. 8 coal (from Penn State Coal Bank: Sample DECS-12) and high purity graphite with iron content less than 5 ppm according to the supplier (from SGL Carbon Inc.) were used during the experiments. In all the experiments the concentrations of coal and graphite were kept constant at 0.02 g/ml. Patil et al. [14] observed approximately twice the current densities due to the synergistic effect of Fe$^{2+}$ and Fe$^{3+}$ on the electrolysis of coal. Because of the promising results obtained by the previous authors 100 mM Fe$^{2+}$ and 100 mM Fe$^{3+}$ in combination were used in the coal and graphite slurries in all the polarization experiments. The particle size of coal and graphite used during the experiments was ranging from 74 - 105 µm.

Before testing, the coal and graphite were stored in an Argon filled Glove box for six months to keep them from exposing to the oxygen which would otherwise form a film on the surface of the coal and graphite. All the experiments were performed galvanostatically at 100 mA until the potential increased to 1.2 V (to avoid water
electrolysis). An ARBIN cycler BT2000 was used to control the current. Figure 11 shows the schematic diagram of the experimental set up.

Figure 11. Schematic diagram of the experimental set up

The CEC was held with the help of a stand. Anodic solution was the slurry of coal/graphite and 1 M H₂SO₄. On the other hand, only 1 M H₂SO₄ was present on the cathode side. This is because; the coal or graphite particles need to be in contact with only the anode [1]. The reactants were stirred with the help of a Fisher Scientific Thermix magnetic stirrer (model 220T). The operating temperature of the reactants was held at 80 °C with the help of thermocouples, J type (Ace Glass) and heating tapes (Fisher
Scientific). The reactants on both sides were circulated in and out of the cell with the help of a Masterflex pump (model 77200-60) at the flow rate of 51.7 ml/min. The flow rate was maintained with the help of a Masterflex speed controller. The gases were collected in measuring cylinders by the method of downward displacement of water (Figure 11). All the gases were collected and analyzed by an SRI gas chromatograph equipped with a thermal conductivity detector, 2 m long HYSEP column, and 1 m long Mole Sieve column. The temperature of the columns was set to change from 30 to 150 °C.

3.4 Results and Discussion

This section discusses the important findings in this research work such as effect of Ir and loading, interaction studies between loading and Ir composition, effect of composition on CO₂ efficiency, effect of graphite on electrooxidation of coal to CO₂, energy consumption for the production of H₂, and stability of coating of noble metals in coal and graphite slurries.

3.4.1 Effect of Ir and Loading on the Performance of the Electrode

Figure 12 shows the effect of iridium and electrode loading on the Faradaic efficiencies for CO₂ during the electrolysis of coal and graphite. The error bars shown were calculated using propagation of errors based on the experimental uncertainties of the potentiostat. The Faradaic efficiency for CO₂ production was calculated by

$$\% \text{ Efficiency} = \frac{\text{Amount CO}_2 \text{ generated}}{\text{Amount CO}_2 \text{ theoretical}} \times 100$$

(8)
where the amount of CO\textsubscript{2} generated represents the total volume of CO\textsubscript{2} measured experimentally. The amount of CO\textsubscript{2} theoretical represents the volume calculated according to Faraday’s law (ideal gas law was assumed and the calculations were performed at 298 K and 1 atm):

\[ V = \frac{SI\textit{t} (RT)}{nF \textit{P}} \]  

(9)

where \( V \) is the theoretical volume of CO\textsubscript{2} (ml), \( S \) is the stoichiometric coefficient of CO\textsubscript{2} (1 mol) in Eq. Error! Reference source not found., \( I \) is the applied current (A), \( t \) is the operating time (h), \( n \) is the number of electrons transferred (4 electrons) in Eq

Figure 12. Effect of Ir and loading on the performance of the electrode (Ir at low and high loadings had negligible effect on coal and graphite oxidation)
Error! Reference source not found., F is Faraday’s constant (26.8 A-h/eq), R is the universal gas constant (82 atm ml/mol K), T is the temperature at which the gas was collected (298 K), and P is the pressure at which the gas was collected (1 atm).

It can be observed that the presence of Ir on the electrolysis of coal at low catalyst loading is negligible. This is evident from efficiency of 2.4 ±0.1 % as compared to 2.4 ±0.3 % when Ir was absent. In the case of graphite also, no difference in the efficiency was found in the absence (3.8 ±0.7 %) or presence of Ir (5.1 ±0.6 %). In other words the presence of Ir did not affect the oxidation of coal and graphite to CO\textsubscript{2} at low catalyst loading. It is important to mention that during the preparation of the slurries it was observed that coal tends to form lumps or agglomerates, and this tendency increases during the electrolysis of coal (possibly due to the formation of films on the surface of the coal particles as reported by others [1, 5, 6]). However, this tendency was not observed in the graphite (the graphite particles stay apart after adding the electrolyte). This may be one of the possible reasons behind higher efficiencies observed for graphite than that for coal in the case of Pt-Rh and Pt-Ir-Rh. It is possible that the preferential catalytic effect of these electrodes might have been overridden by more surface area offered by graphite than by coal (due to the agglomeration tendency) under the same experimental conditions.

Figure 12 also shows the effect of Ir at high electrode loading (9.9 mg/cm) on the oxidation to CO\textsubscript{2}. Even at high catalyst loading, the effect of Ir on the efficiency was found to be insignificant. The efficiencies were essentially found to be the same (4.7 ±0.5 % on Pt-Rh as compared to 6.0 ±1.0 % on Pt-Ir-Rh). In both cases (Pt-Rh and Pt-Ir-Rh)
the efficiency for coal was greater than that for graphite. A possible explanation may be that at high loading the catalytic effect overcomes the agglomeration tendency in the coal. Furthermore, the efficiency on the oxidation of coal at high loadings for both electrode materials was higher than at low loadings (changes from 2.4 ±0.3 % to up to 6.0 ±1.0 % in the efficiency were observed, Figure 12). This is an important observation since it demonstrates the significance of loading in improving the efficiency of the electrolysis of coal slurries towards complete oxidation to CO₂.

It can be observed from Figure 12 that the efficiency for graphite decreased for the electrodes Pt-Rh and Pt-Ir-Rh from loading of 1.7 to 9.9 mg/cm of carbon fiber. This observation is contrary to that observed in the case of coal. However, this anomaly is inexplicable to us at this time. More experiments will be performed in our laboratory to gain a better understanding of the possible reasons behind this unusual trend.

3.4.2 Interaction between Loading (A) and Ir Composition (B)

The interaction between factor A (loading) and B (Ir composition) for the experimental matrix shown in Table 1 was studied by using the concept of factorial design. Figures 13 (a) and 13 (b) show the effects plots for coal and graphite, respectively. The numbers 1 and 2 signify the low and high values for each factor. % CO₂ efficiency is the response variable. Figure 13 (a) shows that the average response is 3.9 %. The response values for loading fall beyond the dotted lines representing the maximum value of uncertainty (0.9 %). This fact indicates that the effect of loading on the CO₂ efficiency is significant from a statistical stand point. This fact is in agreement with the observation made in Section 3.4.1.
Figure 13. Interaction between Loading (A) and Ir Composition (B) for (a) coal and (b) graphite (Factor A was significant in both cases from a statistical stand point)
The effects of Ir composition and the interaction between loading and Ir composition are insignificant because the response values for these effects fall inside the boundaries of the two dotted lines representing the maximum value of uncertainty. Figure 13 (b) shows that the loading of the catalyst is the only significant effect for the electrooxidation of graphite to $\text{CO}_2$ from a statistical point of view. However, this effect is significant in a negative way. It can be seen that the response value at high loading is less than that for low loading. This fact is in agreement with the observation made in Section 3.4.1. The effects of Ir composition and the interaction between loading and Ir composition are insignificant because the response values for these effects fall inside the boundaries of the two dotted lines representing the maximum value of uncertainty (0.7 %).

### 3.4.3 Effect of Electrode Composition on the Electrolysis

Figure 14 shows the comparison of $\text{CO}_2$ Faradic efficiencies for coal and graphite slurries on Pt-Rh, Pt, Rh, Pt-Ir-Rh, and Pt-Ir electrodes with the same noble metal loading (5 mg/cm of carbon fiber). Pt showed no difference in the efficiencies for coal ($8.1 \pm 1.8 \%$) and graphite ($8.9 \pm 1.2 \%$) slurries. The efficiency of Pt-Rh was less for coal ($2.7 \pm 0.6 \%$) than for graphite ($4.5 \pm 0.6 \%$) whereas efficiencies of Rh, Pt-Ir-Rh, and Pt-Ir were greater for coal ($2.9 \pm 0.6 \%, 5.1 \pm 0.8\%$, and $11.3 \pm 2.7 \%$, respectively) than for graphite ($1.9 \pm 0.2 \%, 1.3 \pm 0.2 \%$, and $2.0 \pm 0.3 \%$ respectively). The possible reasons behind these phenomena can again be attributed to the interplay between catalytic effect and surface area of graphite as explained in Section 3.4.1. The preferential catalytic effect of Rh might have been overridden by the surface area that graphite offers under the same
Figure 14. Effect of electrode composition on the electrolysis (Pt and Pt-Ir performed better than all other electrodes at the loading of 5 mg/cm of carbon fiber)

experimental conditions. In case of Pt these two factors might have just counterbalanced each other whereas, for the other electrodes catalytic effect might have exceeded the surface area effect. The efficiencies in the case of coal for Pt-Ir (11.3 ±2.7 %) and Pt (8.1 ±1.8 %) were found to be the same. Patil et al. [14] found that Pt-Ir outperformed all the other electrodes tested in the foil form based on the current density developed in the cell at a given voltage. Our results indicate that from a CO₂ Faradaic efficiency point of view Pt and Pt-Ir outperformed all the other electrodes tested. Our conclusions are some how different because they are based on different comparison criteria.
Rh which was added in the electrode to enhance the plating process unfortunately had an adverse effect on the catalytic activity of the electrodes. Rh in the combination of Pt-Ir-Rh held back Pt-Ir from performing well from an electrochemical point of view. Rh, Pt-Rh, and Pt-Ir-Rh performed poorly compared to Pt and Pt-Ir. This fact shows that Rh alone and also its combination with Pt and Pt-Ir are not good catalysts as they do not favor the electrooxidation of coal to CO₂.

3.4.4 Effect of Graphite on the Electrooxidation of Coal to CO₂

As discussed in Section 3.4.1, graphite particles tend to remain separate even after mixing with water and H₂SO₄, but coal particles tend to agglomerate and form lumps thus reducing the surface area for the reaction. Based on this, it is hypothesized that graphite can serve as a dispersant to enhance the electrooxidation of coal to CO₂. Coal and graphite were mixed in equal proportions (0.01 g/ml of coal and 0.01 g/ml of graphite, in order to achieve a total concentration of 0.02 g/ml of coal-graphite in the slurry) and tested with a Pt-Ir electrode in the CEC under the same experimental conditions. The goal of the experiment was to verify if graphite will help the coal particles to remain suspended during the course of the reaction. The reason behind this is unknown, but it is speculated that the laminar shape of the graphite helps removing some of the films that grow on the surface of the coal during the electrooxidation and that cause agglomeration of the coal particles. Figure 15 shows the performance of coal-graphite combination with Pt-Ir and its comparison with the performance of Pt-Ir and Pt in coal and graphite slurries (all the electrodes had the same noble metal loading, about 5 mg/cm of carbon fiber). It can be seen that the % CO₂ efficiency of the coal-graphite mixture was more than twice
The CO\textsubscript{2} efficiency for the mixture of coal-graphite was 27.8 ± 4.8 %, which is higher than any other value reported in the open literature even at more abrupt conditions (higher coal concentration, electrolyte concentration, and operating temperature than the ones used in this study). Because the efficiency for CO\textsubscript{2} for Pt-Ir for only graphite was less (2.0 ± 0.3 %) than for only coal (11.3 ± 2.7 %), it is unlikely that carbon in graphite in coal-graphite mixture might have contributed strongly for CO\textsubscript{2} generation. The above
discussion suggests that graphite seems to act as a good dispersant to improve the efficiency of the process towards complete oxidation to CO₂.

### 3.4.5 Energy Consumption for the Production of H₂

Figure 16 presents the energy consumption for the production of hydrogen on the CEC using different electrode materials.

**Figure 16. Energy consumption for the production of H₂ from coal and graphite electrolysis at 80 °C** (The energy consumption is about 22 Wh/g of H₂ for all the electrodes tested, 50% lower energy consumption than the electrolysis of water at the same conditions)

In all the calculations, the Faradaic efficiency for the production of H₂ was assumed to be 100 % (since the hydrogen escapes rapidly due to its light weight it was
difficult to quantify, however, previous researchers [1] reported 100% faradaic efficiency for the hydrogen evolution). The results indicate that there is no significant difference in the energy consumption for the production of hydrogen on the different electrode materials. One of the reasons for this behavior may be the mild conditions used during the electrolysis, such as low concentration of coal and graphite as well as low applied current. Additionally, the presence of Fe$^{+2}$ and Fe$^{+3}$ minimizes the consumption of energy as reported by Patil et al [14]. It is important to notice that the current density (25 mA/cm$^2$) obtained for the production of hydrogen was higher than any other value reported on the open literature even at more abrupt operating conditions. The energy consumption for the production of hydrogen is about 22.0 ±1.6 Wh/g of H$_2$, that is, 50% lower energy consumption than the electrolysis of water under similar operating conditions (temperature and current density). This proves that the electrolysis of coal is a competitive technology to be used for the production of hydrogen for distributed power (in-situ hydrogen generators).

3.4.6 Stability of Coating of Noble Metals after the Electrolysis

In the CEC, coal and graphite slurries continuously flow past the carbon fiber electrodes. The coating of noble metals depends on physical forces of attraction between carbon fibers and noble metals since no chemical reaction between the two takes place during the process of plating. Coal and graphite slurries are heterogeneous in nature. Coal and graphite particles are suspended in the slurry and come in contact with the coated fibers during the experiment. As one would imagine it is possible that the coating of noble metals might get eroded away due to the abrasive effect of flowing slurries. To
confirm this fact the electrodes were weighed before and after the experiments. Table 5 shows the % weight loss for different electrodes.

Table 5. % weight loss for different electrodes during the course of experiments. Pt with loading of 5.1 mg/cm of fiber and Pt-Rh with the loading of 5.2 and 9.9 mg/cm of fiber showed significant % loss in weight

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Loading (mg/cm of carbon fiber)</th>
<th>Initial Weight (g)</th>
<th>Final Weight (g)</th>
<th>% Weight Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh</td>
<td>5</td>
<td>0.9684</td>
<td>0.9547</td>
<td>1.4</td>
</tr>
<tr>
<td>Pt</td>
<td>5.1</td>
<td>1.0170</td>
<td>0.8972</td>
<td>11.8</td>
</tr>
<tr>
<td>Pt-Rh</td>
<td>1.7</td>
<td>0.8009</td>
<td>0.7904</td>
<td>1.3</td>
</tr>
<tr>
<td>Pt-Rh</td>
<td>5.2</td>
<td>0.966</td>
<td>0.8735</td>
<td>9.6</td>
</tr>
<tr>
<td>Pt-Rh</td>
<td>9.9</td>
<td>1.0963</td>
<td>0.9244</td>
<td>15.7</td>
</tr>
<tr>
<td>Pt-Ir</td>
<td>5.3</td>
<td>0.8541</td>
<td>0.8458</td>
<td>1.0</td>
</tr>
<tr>
<td>Pt-Ir-Rh</td>
<td>1.7</td>
<td>0.7389</td>
<td>0.7238</td>
<td>2.0</td>
</tr>
<tr>
<td>Pt-Ir-Rh</td>
<td>5.1</td>
<td>0.8930</td>
<td>0.8702</td>
<td>2.6</td>
</tr>
<tr>
<td>Pt-Ir-Rh</td>
<td>9.9</td>
<td>1.0655</td>
<td>1.0380</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Pt with loading of 5.1 mg/cm of carbon fiber showed 11.8 % loss. Pt-Rh with the loadings of 5.2 and 9.9 mg/cm of carbon fiber showed 9.6 % and 15.7 % loss respectively. The % weight loss in the case of these three electrodes is significant when compared to the other electrodes tested. The % weight loss for all other electrodes was found to be in the range of 1–2.6 % which can be considered negligible. Table 5 shows that Rh alone has a very good resistance to erosion of flowing slurries. However, the presence of Pt with Rh reduces the resistance to erosion. The weight loss may be attributed to coming off of Pt coating from the first layer of Rh. The resistance of Pt to erosion seems to improve in the case of the Pt-Ir and Pt-Ir-Rh combinations.
CHAPTER 4: CONCLUSIONS

The following conclusions can be made from the present study:

4.1 Effect of Ir on the Oxidation of Coal and Graphite

At low and high catalyst loadings, Ir had no effect on the oxidation of coal and graphite to CO$_2$.

4.2 Rh does not favor the Electrolysis of Coal Slurry

Rh alone or in the combination with Pt or Pt-Ir does not favor the electrolysis of coal and hence is not recommended. Rh when used with Pt-Ir to form Pt-Ir-Rh actually holds back Pt-Ir from performing well. As the initial matrix gives information on possible negative effects of such a combination, further analysis for this combination is not required. Hence optimization studies for Pt-Ir-Rh need not be performed.

4.3 Pt-Ir as the Best Electrode for the Electrooxidation of Coal to CO$_2$

Ir seems to make a very good combination with Pt. Pt and Pt-Ir performed similarly but outperformed all the other electrodes with the same loading of 5 mg/cm of fiber. However, Pt-Ir seems to be superior to Pt because of an excellent resistance to erosion. Hence, Pt-Ir seems to be the best electrode for the conversion of coal to CO$_2$ (from a CO$_2$ Faradaic efficiency point of view).

4.4 Graphite as a Good Dispersant

Graphite seems to act as a good dispersant. When it was used in coal-graphite mixture, it seemed to have a positive effect on improving the surface area of coal in the mixture. This can be verified from the fact that coal-graphite mixture for Pt-Ir gave more than twice CO$_2$ efficiency than Pt and Pt-Ir in only coal.
4.5 Energy Consumption of Hydrogen Production

Energy consumption of hydrogen production was found to be almost the same for all electrode materials. However, the value of 22 Wh/g of H$_2$ is 50 % lower than that for hydrogen production by electrolysis of water under similar operating conditions (temperature and current density). This fact shows that coal electrolysis is a competitive method for *in-situ* hydrogen generation.

4.6 Effect of Erosion on Noble Carbon Fiber Electrodes

Pt with loading of 5.1 mg/cm of carbon fiber and Pt-Rh with the loadings of 5.2 and 9.9 mg/cm of carbon fiber were influenced by flowing slurries of coal and graphite and showed the negative effect of erosion. They lost valuable coating of noble metals during this erosive effect. However, Pt with Ir showed an improved resistance to erosion. Rh seems to have a very good adherence with carbon fibers since Rh coating was never observed to come off due to erosion.
CHAPETR 5: FUTURE WORK

In the course of this research, numerous improvements to the experimental design were discovered. This chapter details recommendations to be considered in order to improve future studies.

5.1 Optimization Studies for Pt-Ir

Pt-Ir with loading of 5.1 mg/cm of carbon fiber seems to be the best electrode material because of its excellent catalytic properties and good resistance to erosion. Factorial design can be used to further investigate the effect of loading and composition on CO$_2$ efficiency. Preliminary matrix similar to that presented in Chapter 3 (Table 1) can be prepared. This would help to determine if there exists any interaction effect between the above two factors and design the experimental matrix to find the optimum loading and composition.

5.2 Effect of Coal Concentration

Higher coal concentrations may be tested in future. Coughlin and Farooque [3] reported a positive effect of increase in coal concentration on the oxidation rate of coal.

5.3 Different Ranges of Operating Parameters

Stronger operating parameters can be used in order to improve the efficiency of the process. Higher values of H$_2$SO$_4$ concentration, temperature, smaller particle size can be tested.

5.4 Researching a Cheaper Dispersant

Graphite was found to be a very good dispersant. However, a cheaper substitute
for graphite should be researched. This material should not undergo electrochemical oxidation and have excellent surface properties. Breakthrough in this area would be a major leap in this research because the surface area of coal can be enhanced by preventing its agglomeration.

5.5 Improved Experimental Apparatus

It is hypothesized that hydrogen being lighter than air escapes very quickly to the atmosphere and is difficult to collect. Better design for capture of $\text{H}_2$ is needed to get good data for $\text{H}_2$ collection.
REFERENCES


