

Assessment of coal and graphite electrolysis on carbon fiber electrodes

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Abstract

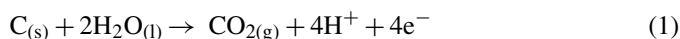
Novel carbon fiber electrodes prepared by plating of noble metals (Pt, Rh, Pt–Rh, Pt–Ir, Pt–Ir–Rh) on carbon fibers were evaluated for the electrolysis of coal and graphite under galvanostatic conditions. Graphite was used as a baseline to compare its performance with coal. The electrodes were tested on a sandwich configuration coal electrolytic cell (CEC) designed to reduce the ohmic resistance of the system. Among Pt, Rh, Pt–Rh, Pt–Ir, and Pt–Ir–Rh electrodes with the same loading (5 mg cm^{-1} of fiber bundle), Pt and Pt–Ir seemed to produce the highest CO_2 Faradaic efficiency. Factorial design was 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 was determined by performing weight change analysis. Most electrodes were not significantly affected by abrasive effect (about 2% weight loss); however, Pt and Pt–Rh electrodes were significantly affected by erosion (above 10% weight loss). The presence of graphite had 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 was about 22 Wh g^{-1} 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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1. Introduction

In 1979, Coughlin and Farooque introduced the process of electrolysis of coal slurries [1], the authors proposed the following reactions:



where reactions (1) and (2) take place at the anode and cathode, respectively. The electrochemical gasification of coal slurries to produce H_2 is thermodynamically more favorable than water electrolysis for that purpose. Electrochemical gasification of coal slurries requires only 0.21 V of standard driving potential as compared to water electrolysis, which takes place at a standard potential of 1.23 V. The electrolysis of coal slurry requires only 9.5 kcal of electrical energy per mole of H_2 as compared to 56.7 kcal per mole for the electrolysis of water. Because of the simplicity of the reactions and the low temperature of operation,

the electrolysis of coal could find applications in distributed power and small hydrogen generators [2]. The main research challenge in this regard is that even if the process looks very attractive from a thermodynamics point of view, it is not kinetically favorable.

Several authors [3–13] had performed different studies related to electrooxidation of coal slurries. These studies were focused on different aspects such as: (1) effect of various parameters like temperature, particle size, concentration of coal slurries, and concentration of H_2SO_4 on the electrooxidation of coal, (2) reaction mechanism, (3) removal of sulfur and ash in coal via electrolysis in acidic and basic media, and (4) electrolysis of different types of coals.

Farooque and Coughlin [3] studied the effect of particle size, coal concentration, temperature, and supporting electrolyte on the electrooxidation of coal. They also determined the activation energy of the reaction and performed different studies at galvanostatic conditions. The same researchers [5] also analyzed different elements (C, H, O, N, S etc.) present in several coals (North Dakota Lignite, Pittsburgh Seam Coal, and Minnesota Red Sedge Peat) before and after the electrolysis. Murphy and Bockris [8] tested lignite washed with water and also the filtrate

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of the slurry by using Sep-pak cartridges. They concluded that the current was influenced by pH, electrocatalysts, abrasion of coal particles, and intermediate redox reactions. Baldwin et al. [9] studied the voltametric and electrolytic behavior of several coal slurries and H-coal liquids in aqueous as well as in organic solvents. Dhooge et al. [10] proposed that iron ions leached out of coal are major responsible for the anodic currents. Dhooge and Park [11] proposed that carbon dioxide is formed through the formation of oxygen compounds on the coal surface and studied the effect of various reactive couples (Fe^{2+} – Fe^{3+} , Ce^{3+} – Ce^{4+}) on the reaction rate.

Coughlin and Farooque [1] and Okada et al. [7] investigated the electrolysis of graphite in order to have a better understanding of the electrolysis of coal. Graphite was chosen, as it is one of the pure forms of carbon. The oxidation currents observed with graphite were an order of magnitude lower than that of coal, which was due to the inert nature of graphite.

Recently, Patil et al. [2] investigated the electrooxidation of coal slurries on different electrode materials. The authors reported that Pt–Ir seems to be the best electrode (based on the current densities developed during potentiostatic experiments) 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 no separator membrane.

All the results reported in the open literature on the electrolysis of coal have been performed in batch glass cells. Typical cells 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_2SO_4 salt bridge [10]. 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:

1.1 Evaluate the performance of noble metals deposited on carbon fibers substrates (noble-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 [14] 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. [2], 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 [14] 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. [2] and Botte [14], 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_2 Faradaic efficiency) among them.

- 1.2 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 metal-carbon fiber electrode composition on the electrolysis of coal. This method makes sure that the interaction factors are also taken into account.
- 1.3 Compare the electrochemical performance of graphite with coal for all the electrodes mentioned in 1.1 and 1.2 to determine whether the surface structure of them plays an important role in the difference between their electrochemical activities. This difference was measured by calculating CO_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.

2. Experimental design

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 [15]. 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. Factor A represents loading (in mg of noble metal cm^{-1} of carbon fiber bundle) and has two values, 1.7 and 9.9 representing low and high levels, respec-

Table 1
Experimental design to evaluate the effect of loading (factor A, mg of noble metal cm^{-1} of carbon fiber bundle) and Ir content (factor B, % Ir present in total Pt–Ir mass on the carbon fibers, Pt–Ir mass was 70% of noble metal loading) on the electrolysis of coal and graphite

| Trial | Electrode | Factors | |
|-------|---------------|---------|------|
| | | A | B |
| 1 | Pt–Rh(1.7) | Low | Low |
| 2 | Pt–Ir–Rh(1.7) | Low | High |
| 3 | Pt–Rh(9.9) | High | Low |
| 4 | Pt–Ir–Rh(9.9) | High | High |

An orthogonal factorial design was used for the experimental matrix. Each factor had two levels, low and high. For factor A low level was 1.7 mg cm^{-1} and high level was 9.9 mg cm^{-1} of carbon fiber bundle. For factor B low and high levels were 0% Ir and 70% Pt–Ir, respectively.

Table 2

Experimental matrix, which comprises the electrodes tested: Rh, Pt–Rh, Pt, Pt–Ir, Pt–Ir–Rh. The total loading was set at 5 mg cm^{-1} of carbon fiber bundle. The electrodes in which Rh is one of the constituents (Pt–Rh, Pt–Ir–Rh) have 30% by weight of Rh

| Number | Electrode | Loading (mg cm^{-1} of fiber) |
|--------|-----------|---|
| 1 | Rh | 5.0 |
| 2 | Pt–Rh | 5.2 |
| 3 | Pt | 5.1 |
| 4 | Pt–Ir | 5.3 |
| 5 | Pt–Ir–Rh | 5.1 |

tively. All the loadings mentioned are per cm of carbon fiber bundle (see Section 2.2 for more details), since the carbon fibers bundles could be extended or reduced to different supports, it is more accurate to report the loading per cm of carbon fiber bundle. Factor B represents percentage of 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 metal-carbon fiber electrode for the electrooxidation of coal slurry to CO_2 . Patil et al. [2] 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 [2] was based on the current density generated on the cell at a given voltage and they did not consider the Faradaic CO_2 efficiency. It was a major interest to determine whether Pt–Ir performed better than all the other electrode materials (in terms of the Faradaic CO_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 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^{-1} of carbon fiber bundle). The electrodes in which Rh is one of the constituents (Pt–Rh, Pt–Ir–Rh) have 30% Rh by weight of total loading.

2.2. Preparation of electrodes

The base support of the electrode was made up of $2 \text{ cm} \times 2 \text{ cm}$, 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

Table 3

Order of plating of different noble metals on the carbon fiber electrodes

| Electrode | Order of plating |
|-----------|--|
| Pt | Pt |
| Rh | Rh |
| Pt–Rh | First layer Rh second layer Pt |
| Pt–Ir–Rh | First layer Rh second layer Pt–Ir (co-deposited) |
| Pt–Ir | One layer, Pt–Ir were co-deposited |

wire (0.81 mm o.d., 15 cm long with a purity of 99.7% on metals basis) so that the resistance across the joint was low ($0.2\text{--}0.3 \Omega$). Titanium is also resistant to corrosive acidic media at the operating temperature. Polyacrylonitrile (PAN) based carbon fibers (Celion G30-500, $7 \mu\text{m}$ diameter) were obtained from BASF and were used as 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 fibers were then fixed to the stem with the help of a small titanium clip. Fig. 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 Ti gauze earlier wound with carbon fibers were directly plated in a Pt solution bath. 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 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 plating conditions 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 H_2PtCl_6 to achieve a concentration of 0.8 mg ml^{-1} (Table 4) in 1 M HCl (prepared using ultra high

Table 4

Important experimental parameters for plating of Rh, Pt, and Pt–Ir on the carbon fiber electrodes

| Parameters | Rh | Pt | Pt–Ir |
|--|---|---|---|
| Salt | RhCl_3 | H_2PtCl_6 | $\text{H}_2\text{PtCl}_6 + \text{IrCl}_3$ |
| Chemicals | 1 M HCl prepared with ultra high purity water | 1 M HCl prepared with ultra high purity water | 1 M HCl prepared with ultra high purity water |
| Concentration of salt (mg ml^{-1}) | 0.5 | 0.8 | 0.4, 1.04 |
| Temperature of plating bath ($^\circ\text{C}$) | 80 | 80 | 80 |
| Current (mA) | 100 | 100 | 250 |
| Voltage range (V) | -1.2 to -1.3 | -1.1 to -1.2 | -0.8 to -1.3 |

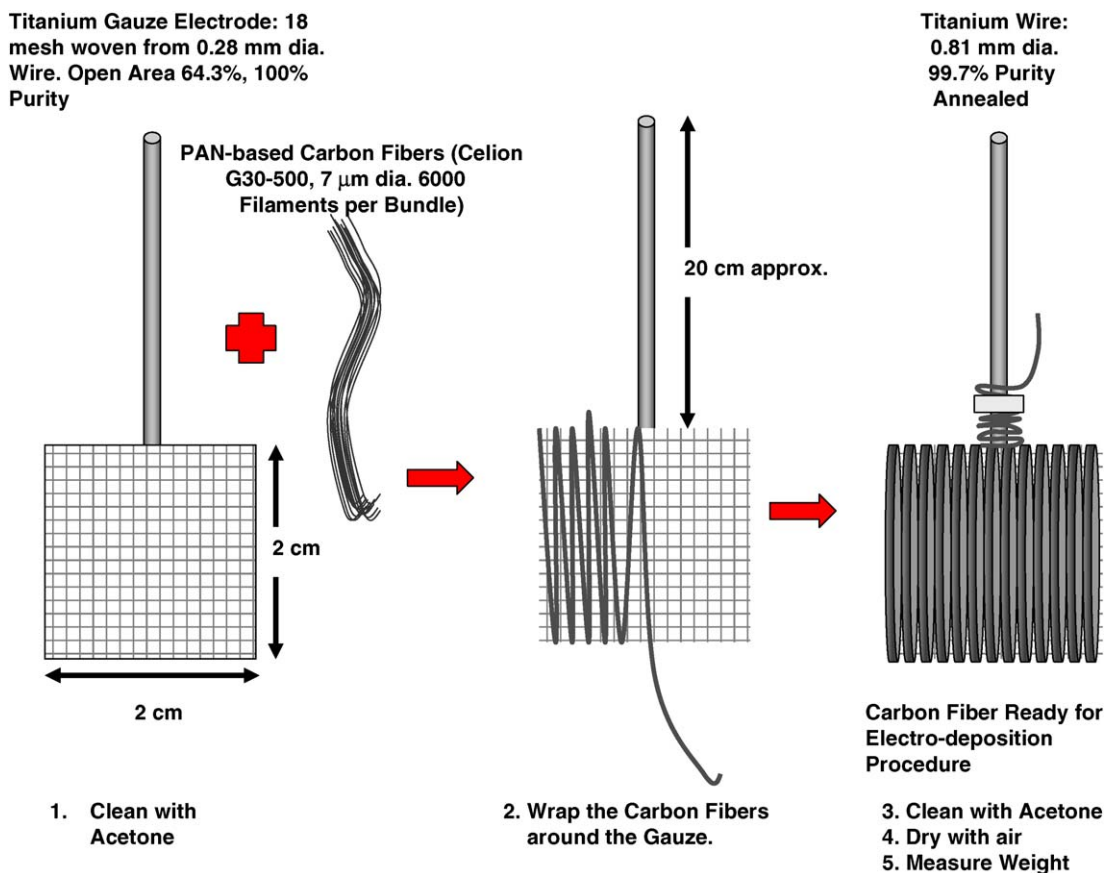


Fig. 1. Schematic representation of the procedure used for the preparation of the carbon fiber electrodes (originally drawn by Elizabeth Cellar, undergraduate research student at the EERL Ohio University). Titanium gauze is used as a current collector to increase the electronic conductivity of the fibers.

pure 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 Pt electrodeposition was carried out galvanostatically at 100 mA in intervals of 20–30 min (Table 4). An ARBIN cyclor BT2000 was used to control the current. During the process, it was ensured that the voltage range remained between -1.1 and -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. The electrodes were thoroughly cleaned with 1 M HCl solution in an ultrasonic bath before taking the SEM images. Fig. 2 shows the scanning electron micrographs (SEMs) of different electrodes before testing in coal and graphite slurries. Fig. 2a shows the SEM of Rh with loading of 5.2 mg cm^{-1} of carbon fiber bundle. 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. Fig. 2b shows the SEM of Pt with loading of 5.1 mg cm^{-1} of carbon fiber bundle. It can be seen that the morphology of Pt coating is different from Rh. Plating of Pt gave sharp granules or dots as compared to flat coating with Rh. However, all the carbon fibers were completely and uniformly covered. Fig. 2c shows SEM of Pt–Ir–Rh with loading of 1.7 mg cm^{-1} of carbon fiber bundle. 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^{-1} of carbon fiber bundle, Fig. 2d) more fibers were coated and also, the density of Pt–Ir dots increased. At high loading, 9.9 mg cm^{-1} of carbon fiber bundle, Pt–Ir–Rh (Fig. 2e) shows increasing trend in the density of dots and the coverage of fibers. In this case only a small fraction of fibers were not covered with noble metal. Fig. 2f–h represent Pt–Rh at low (1.7 mg cm^{-1} of carbon fiber bundle), medium (5.2 mg cm^{-1} of carbon fiber bundle), and high (9.9 mg cm^{-1} of carbon fiber bundle) loadings, respectively. Similar observation in terms of coatings can be made as in the case of Fig. 2c–e, respectively. However, in the case of medium loading of Pt–Rh an unusual morphology of Pt was observed, which can be attributed to high concentration of catalysts at the edge of electrode.

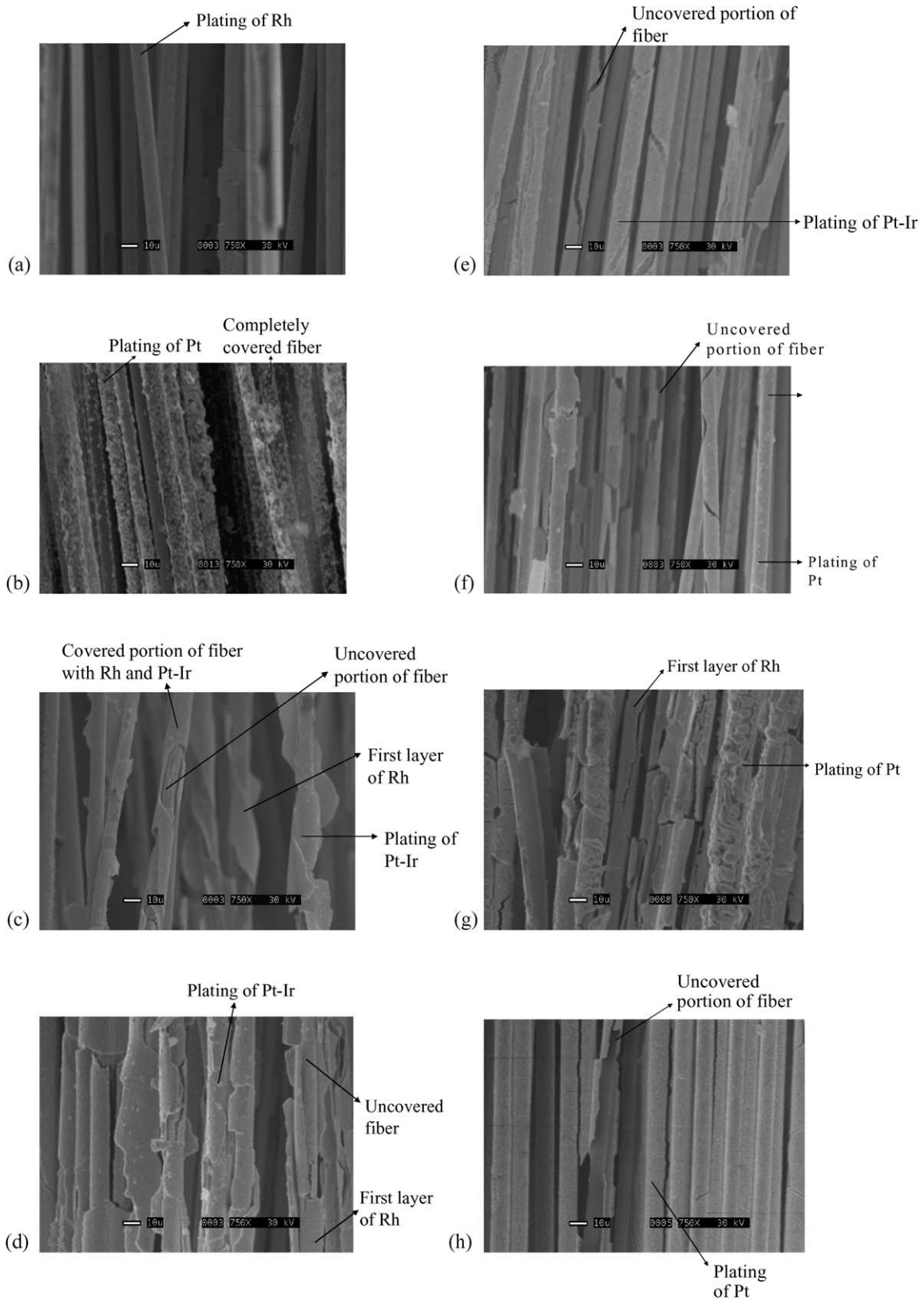


Fig. 2. Scanning electron micrographs of electrodes before testing in coal and graphite slurries. (a) Rh-5.2 mg cm⁻¹ of fiber bundle, (b) Pt-5.1 mg cm⁻¹ of fiber bundle, (c) Pt-Ir-Rh-1.7 mg cm⁻¹ fiber bundle, (d) Pt-Ir-Rh-5.1 mg cm⁻¹ fiber bundle, (e) Pt-Ir-Rh-9.9 mg cm⁻¹ of fiber bundle, (f) Pt-Rh-1.7 mg cm⁻¹ fiber bundle, (g) Pt-Rh-5.2 mg cm⁻¹ of fiber bundle, and (h) Pt-Rh-9.9 mg cm⁻¹ fiber bundle. Morphology of coating of Rh was found to be flat where as Pt and Pt-Ir gave rise to coating in the form of dots or granules.

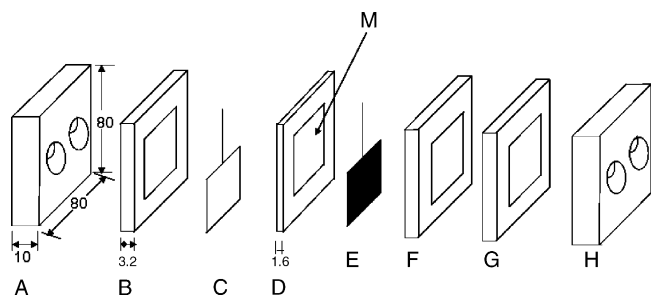


Fig. 3. Schematic representation of the coal electrolytic cell (CEC). A cell assembly in sandwich configuration was used. The parts of the cell include: polycarbonate plates (A and H), Teflon gaskets (B, D, F, and G), carbon fiber electrodes (C: counter electrode, Pt, 9.1 mg cm^{-1} of fiber bundle and E: working electrode), and membrane (M). All dimensions shown are given in mm.

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 Fig. 3. Polycarbonate plates (80×80 , 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 (see Fig. 4) 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 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^{-1} carbon fiber bundle (this electrode was made by electrodeposition using the procedure described in Section 2.2). 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 having an extra gasket on the anode side was to provide an extra space for the flow of coal/graphite slurry over the electrode surface to prevent the accumulation of coal/graphite particles in the pockets formed between the membrane and gasket. The two polycarbonate plates were then tightened together with the help of four screws.

The advantages of the sandwich cell configuration described above are:

- (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. Experimental conditions and methodology

The polarization experiments were carried out in the CEC shown in Fig. 3. Sulfuric acid was used as the electrolyte with a concentration of 1 M. Pittsburgh No. 8 coal (Penn State Coal Bank: Sample DECS-12) and high purity graphite with iron content less than 5 ppm according to the supplier (SGL Carbon Inc.) were used during the experiments. In all the experiments

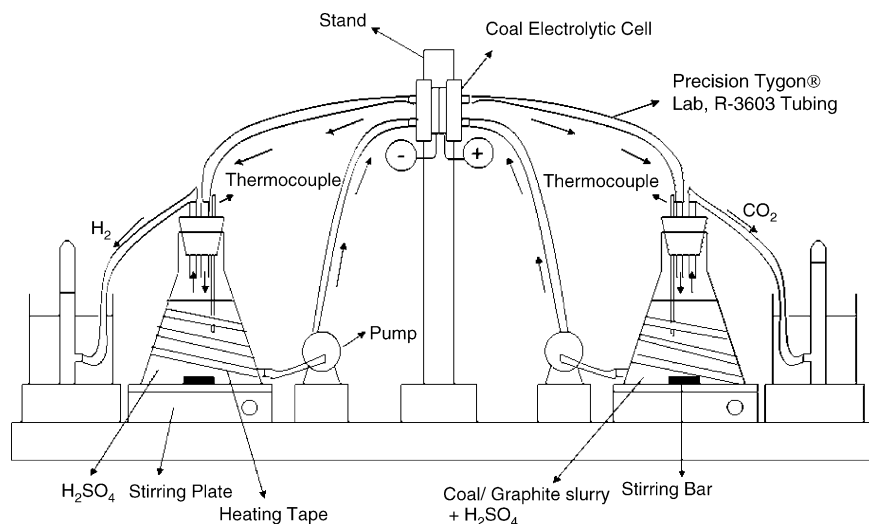


Fig. 4. Schematic diagram of the experimental set-up.

the concentrations of coal and graphite were kept constant at 0.02 g ml^{-1} . Patil et al. [2] 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 for the polarization experiments. The particle size of coal and graphite used during the experiments was ranging from 74 to $105 \mu\text{m}$.

Before testing, the coal and graphite were stored in an Argon filled Glove box for 6 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 (25 mA cm^{-2}) until the potential reached 1.2 V (to avoid water electrolysis). An ARBIN cycler BT2000 was used to control the current. Fig. 4 shows the 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 $1 \text{ M H}_2\text{SO}_4$. On the other hand, only $1 \text{ M H}_2\text{SO}_4$ was present on the cathode side, because the coal or graphite particles need to be in contact with the anode [1]. The volume of solution used for the anode and cathode reservoirs was 200 ml . If only Fe^{+2} ions were oxidized at the anode compartment, the polarization time of the cell (for the applied current) should have been 5.4 h according to Faraday's law assuming 100% efficiency (see Section 4.7), while the polarization time in all the electrode combinations was about 6.3 h (see Section 4.7). 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 a flow rate of 51.7 ml min^{-1} , which was maintained by a Masterflex speed controller. The coal and/or graphite solutions were circulated several times, because the CEC was not designed to oxidize more coal in a shorter time. The gases were collected in measuring cylinders by the method of downward displacement of water (Fig. 4). 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 Molecular Sieve column. The temperature of the columns was set to change from 30 to 150°C .

4. Results and discussion

4.1. Effect of Ir and loading on the performance of the electrode

Fig. 5 shows the effect of iridium and electrode loading on the Faradaic efficiencies for CO_2 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 CO_2 production was calculated by

$$\% \text{efficiency} = \frac{\text{amount CO}_2 \text{ generated}}{\text{amount CO}_2 \text{ theoretical}} \times 100 \quad (3)$$

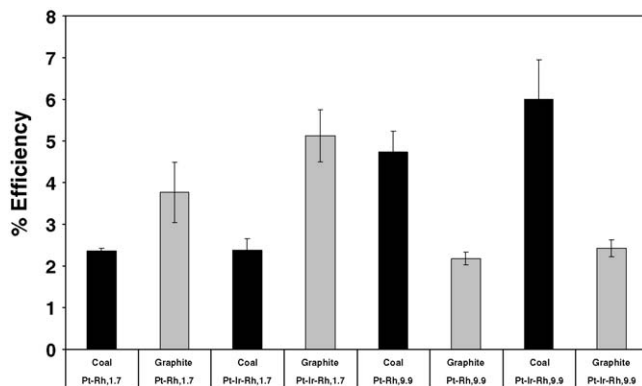


Fig. 5. Effect of Ir and loading on the electrooxidation of coal and graphite to CO_2 . Ir at low and high loading had negligible effect on coal and graphite oxidation.

where the amount of CO_2 generated represents the total volume of CO_2 measured experimentally. The amount of CO_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):

$$V = \frac{SI}{nF} \left(\frac{RT}{P} \right) \quad (4)$$

where V is the theoretical volume of CO_2 (ml), S is the stoichiometric coefficient of CO_2 (1 mol) in Eq. (1), I is the applied current (A), t is the operating time (h), n is the number of electrons transfer (four electrons) in Eq. (1), F is Faraday's constant (26.8 Ah/equiv.), R is the universal gas constant ($82 \text{ atm ml mol}^{-1} \text{ K}^{-1}$), 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 an efficiency of $2.4 \pm 0.1\%$ as compared to $2.4 \pm 0.3\%$ when Ir was absent. In the case of graphite also, no significant difference in the efficiency was found in the absence ($3.8 \pm 0.7\%$) or presence of Ir ($5.1 \pm 0.6\%$). In other words the presence of Ir did not affect the oxidation of coal and graphite to CO_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 [1,7,9]. However, this tendency was not observed with graphite (the graphite particles did not agglomerate in 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 the more surface area offered by graphite than by coal (due to the agglomeration tendency) under the same experimental conditions.

Fig. 5 also shows the effect of Ir at high electrode loading (9.9 mg cm^{-2} of carbon fiber bundle) on the oxidation of coal and graphite to CO_2 . Even at high catalyst loading, the effect of Ir on the efficiency was found to be insignificant. The effi-

ciencies were essentially found to be the same ($4.7 \pm 0.5\%$ on Pt–Rh as compared to $6.0 \pm 1.0\%$ on Pt–Ir–Rh). In both cases (Pt–Rh and Pt–Ir–Rh) the efficiency for coal was greater than that for graphite. It could be possible 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 $2.4 \pm 0.3\%$ to up to $6.0 \pm 1.0\%$ in the efficiency were observed, Fig. 5). 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 CO_2 .

Fig. 5 also illustrates that the efficiency for graphite decreased for the electrodes Pt–Rh and Pt–Ir–Rh from loading of $1.7\text{--}9.9 \text{ mg cm}^{-1}$ of carbon fiber bundle. This observation was contrary to the conclusion derived in the case of coal. However, this anomaly is inexplicable to us at this time. More experiments will be performed to gain a better understanding of this unusual behavior.

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. Fig. 6a and b show the

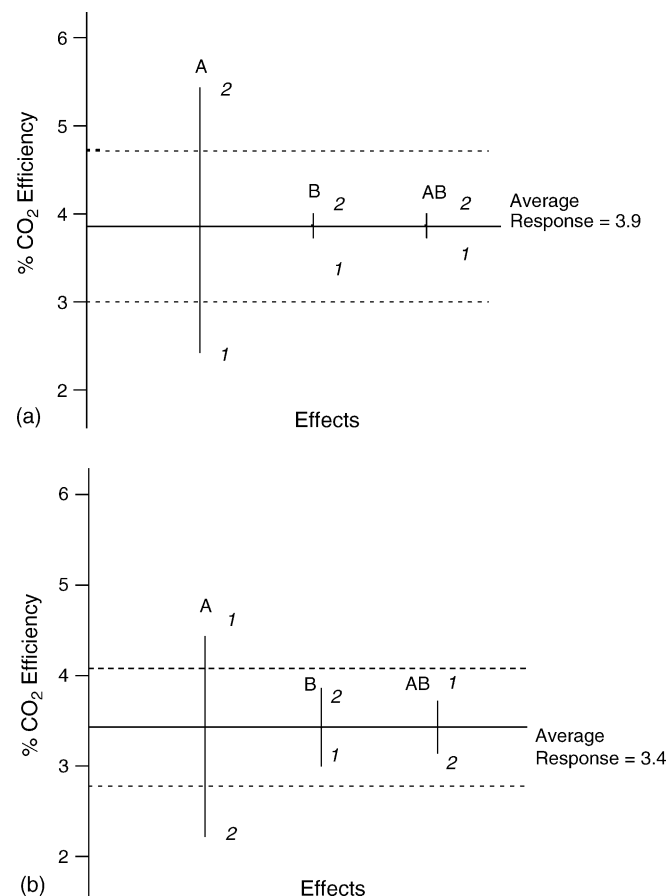


Fig. 6. Interaction between loading (A) and Ir composition (B) for (a) coal and (b) graphite. Factor A was significant in both cases from a statistical stand point.

effects plots for coal and graphite, respectively. The numbers 1 and 2 signify the low and high values for each factor. Percentage of CO_2 efficiency is the response variable. Fig. 6a shows that the average response is 3.9%. The response values for loading fell beyond the dotted lines representing the maximum value of uncertainty (0.9%), which indicates that the effect of loading on the CO_2 efficiency is significant from a statistical stand point. This fact is in agreement with the observation made in Section 4.1. The effects of Ir composition as well as the interaction between loading and Ir composition are insignificant because the response values for these effects fell inside the boundaries of the two dotted lines representing the maximum value of uncertainty. Fig. 6b displays that the loading of the catalyst was the only significant effect for the electrooxidation of graphite to CO_2 from a statistical point of view. However, this effect was significant in a negative way. It can be seen that the response value at high loading was less than that for low loading. This fact is in agreement with the observation made in Section 4.1. The effects of Ir composition as well as the interaction between loading and Ir composition are insignificant because the response values for these effects fell inside the boundaries of the two dotted lines representing the maximum value of uncertainty (0.7%).

4.3. Effect of electrode composition on the electrolysis

Fig. 7 shows the comparison of CO_2 Faradaic 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^{-1} of carbon fiber bundle). 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 on coal ($2.7 \pm 0.6\%$) than on graphite ($4.5 \pm 0.6\%$) whereas efficiencies of Rh, Pt–Ir–Rh, and Pt–Ir were greater on coal ($2.9 \pm 0.6\%$, $5.1 \pm 0.8\%$, and $11.3 \pm 2.7\%$, respectively) than on graphite ($1.9 \pm 0.2\%$, $1.3 \pm 0.2\%$, and $2.0 \pm 0.3\%$, respectively). These phenomena can be attributed to the interplay between catalytic effect and surface area of graphite as explained in Section 4.1. The preferential catalytic effect of Rh might have been overridden by the surface area that graphite offers under the same experimental conditions. In case of Pt these two factors might have just counterbalanced each other whereas,

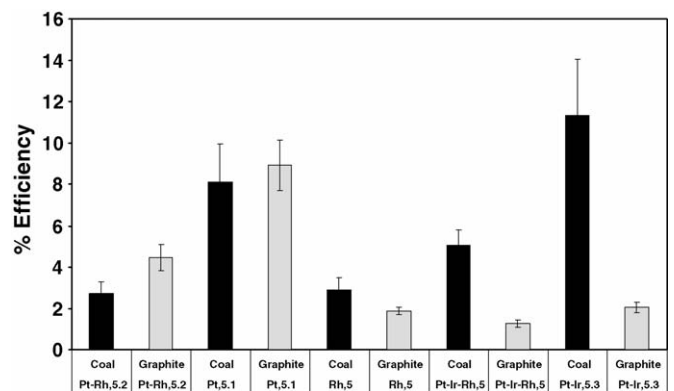


Fig. 7. Effect of electrode composition on the electrooxidation of coal and graphite to CO_2 . Pt–Ir and Pt performed better than all other electrodes at the loading of 5 mg cm^{-1} of carbon fiber bundle.

for the other electrodes catalytic effect might have exceeded the surface area effect. The efficiencies in the case of coal for Pt–Ir ($11.3 \pm 2.7\%$) and Pt ($8.1 \pm 1.8\%$) electrodes were found to be very similar. Patil et al. [2] 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 included in the electrode to enhance the plating process, but 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, which indicates that Rh alone and also in combination with Pt and Pt–Ir was not a good catalyst to favor the electrooxidation of coal to CO₂.

4.4. Effect of graphite on the electrooxidation of coal to CO₂

As discussed in Section 4.1, graphite particles tend to remain separated 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 was 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^{-1} of coal and 0.01 g ml^{-1} of graphite, in order to achieve a total concentration of 0.02 g ml^{-1} 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. Fig. 8 shows the per-

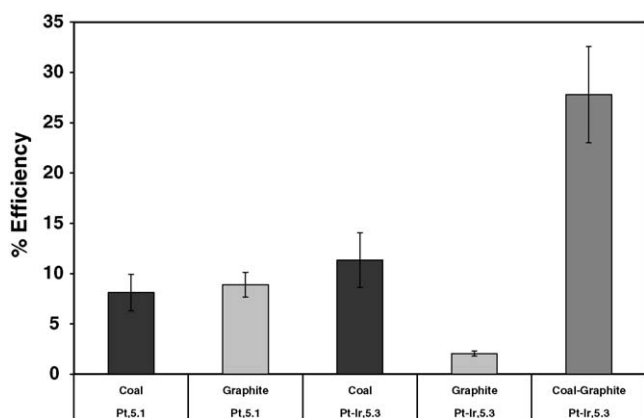


Fig. 8. Effect of graphite on the electrooxidation of coal to CO₂. The mixture of coal–graphite in slurry for Pt–Ir showed more than twice the efficiency than that of Pt and Pt–Ir in only coal.

formance 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^{-1} of carbon fiber bundle). It can be seen that the percentage of CO₂ efficiency for the coal–graphite mixture was more than twice the efficiency obtained for coal from Pt and Pt–Ir electrodes. This suggests that coal might have remained in suspension and gave higher efficiency value even at lower concentration. The CO₂ efficiency for the mixture of coal–graphite was $27.8 \pm 4.8\%$, 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 CO₂ efficiency of Pt–Ir electrode on graphite was less ($2.0 \pm 0.3\%$) than for coal alone ($11.3 \pm 2.7\%$), it was unlikely that the carbon in graphite (coal–graphite mixture) might have contributed strongly to the CO₂ 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.

4.5. Energy consumption for the production of H₂

Fig. 9 presents the energy consumption for the production of hydrogen on the CEC using different electrode materials. 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 was 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. [2]. It is important to notice that the current density (25 mA cm^{-2}) obtained for the production of hydrogen was

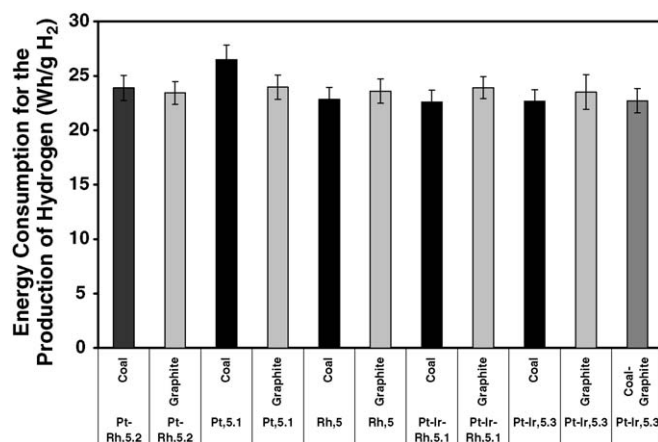


Fig. 9. Energy consumption for the production of H₂ from coal and graphite electrolysis at 80 °C. The energy consumption is about 22 Wh g^{-1} of H₂ for all the electrodes tested (50% lower energy consumption than the electrolysis of water at the same conditions).

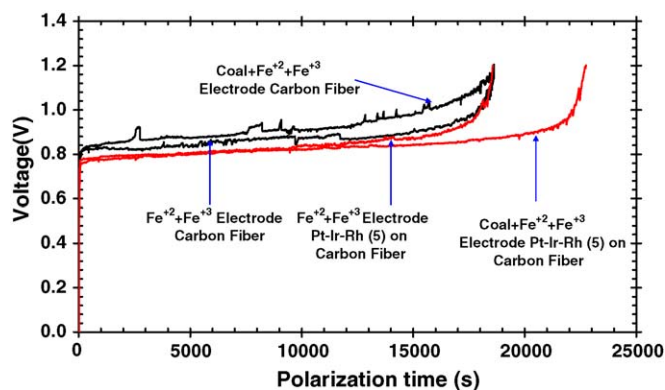


Fig. 10. Effect of coal and anode electrode composition on the electrochemical performance of the CEC. The plated electrode contains Pt–Ir–Rh (5.1 mg cm^{-1} of carbon fiber bundle, see Table 2). All the experiments were performed at 80°C with $1 \text{ M H}_2\text{SO}_4$ electrolyte, 100 mM Fe^{+2} and 100 mM Fe^{+3} . CO_2 was not detected when carbon fiber electrodes were used as anode in the CEC, which indicates that the fibers do not oxidize in the process. The experiment performed with coal using the plated anode electrode showed an elapsing time longer than without the presence of coal.

higher than any other value reported on the open literature even at more abrupt operating conditions. The energy consumption for the production of hydrogen was about $22.0 \pm 1.6 \text{ Wh g}^{-1}$ 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). The energy calculations reported do not include the energy consumed by the pumps (the polarization time in all the electrode combinations was about 6.3 h, see Fig. 10), since in a large scale system the CEC should be designed to oxidize more coal in a shorter period of time.

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 them 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, the electrodes were weighed before and after the experiments. Table 5 shows the percentage of weight loss for different electrodes. Pt with a loading of 5.1 mg cm^{-1} of carbon fiber bundle showed 11.8% loss, whereas Pt–Rh with loadings of 5.2 and 9.9 mg cm^{-1} of carbon fiber bundle showed 9.6% and 15.7% loss, respectively. The percentage of weight loss in the case of these three electrodes is significant when compared to the other electrodes tested. The percentage of weight loss for all other electrodes was found to be in the range of 1–2.6%, which can be considered negli-

Table 5

Weight loss for the electrodes during the course of the experiments

| Electrode | Loading (mg cm^{-1} of carbon fiber) | Initial weight (g) | Final weight (g) | %Weight loss |
|-----------|--|--------------------|------------------|--------------|
| Rh | 5 | 0.9684 | 0.9547 | 1.4 |
| Pt | 5.1 | 1.0170 | 0.8972 | 11.8 |
| Pt–Rh | 1.7 | 0.8009 | 0.7904 | 1.3 |
| Pt–Rh | 5.2 | 0.966 | 0.8735 | 9.6 |
| Pt–Rh | 9.9 | 1.0963 | 0.9244 | 15.7 |
| Pt–Ir | 5.3 | 0.8541 | 0.8458 | 1.0 |
| Pt–Ir–Rh | 1.7 | 0.7389 | 0.7238 | 2.0 |
| Pt–Ir–Rh | 5.1 | 0.8930 | 0.8702 | 2.6 |
| Pt–Ir–Rh | 9.9 | 1.0655 | 1.0380 | 2.6 |

Pt (5.1 mg cm^{-1}) and Pt–Rh (5.2 and 9.9 mg cm^{-1}) electrodes showed significant loss in weight.

ble. Table 5 shows that Rh alone has a very good resistance to erosion from flowing slurries. However, the presence of Pt with Rh reduces the resistance to erosion. The weight loss may be attributed to the falling 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.

4.7. Blank experiments and galvanostatic performance

As described in Section 3, all the polarization experiments were performed at 100 mA until the cell voltage increased to 1.2 V . Fig. 10 shows the voltage of the CEC as a function of time. As time elapses the voltage of the cell increases because the concentration of the species, which can be electrooxidized decreases. Several conclusions can be drawn from this figure. Experiments with only Fe^{+2} and Fe^{+3} (100 mM each) were performed to compare with the electrolysis of coal/ $\text{Fe}^{+2}/\text{Fe}^{+3}$ slurry. Two different anode electrode compositions are compared. One of the electrodes contains only carbon fibers (fabricated as explained in Section 2.2, without plating) and the other electrode contains Pt–Ir–Rh (5.1 mg cm^{-1} of carbon fiber bundle, see Table 2). The figure indicates that the electrooxidation of coal does not take place on the electrode with only carbon fibers, since the polarization time for the cell was only 5.2 h, which is almost the theoretical time for the electrooxidation of Fe^{+2} according to Faraday's law assuming 100% efficiency (5.3 h). Furthermore, CO_2 was not detected (using the measuring method described in Section 3) during the polarization of the CEC using the electrode with only carbon fibers as anode (with and without coal in solution), which indicates that the carbon fibers are not oxidized during the process.

The experiment performed with coal using the plated electrode as anode showed an elapsing time of 6.3 h which is longer than when coal was not present, and this indicates that as coal was oxidized, Fe^{+3} was reduced to Fe^{+2} , as proposed by Patil et al. [2]. It can be observed, that the cell potential was constant at about 0.82 V during the testing time. However, the potential increased suddenly after a certain time. This result is related with the loss of reactivity of the coal particles due to the formation or accumulation of products on the surface of coal as reported by others [11].

5. Conclusions

The electrolysis of coal and graphite was evaluated under galvanostatic conditions on different novel carbon fiber electrodes prepared by plating of noble metals (Pt, Rh, Pt–Rh, Pt–Ir, Pt–Ir–Rh) on carbon fibers. Graphite was used as a baseline to compare its performance with coal. The electrodes were tested on a sandwich configuration coal electrolytic cell (CEC) designed to reduce the ohmic resistance of the system. The effect of catalyst loading and iridium content on the electrolysis of coal and graphite was also determined. It was found that at low and high catalyst loadings, Ir had no effect on the oxidation of coal as well as graphite to CO₂. Rh alone or in combination with Pt or Pt–Ir did not favor the electrolysis of coal and hence is not recommended. Ir seems to make a very good combination with Pt for the oxidation of coal to CO₂. Pt–Ir and Pt outperformed all other electrodes with the same loading. 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 CO₂ (from a CO₂ Faradaic efficiency point of view).

Graphite seems to act as a good dispersant agent to enhance the electrooxidation of coal to CO₂. Probably, the laminar shape of the graphite helped in removing some of the films that grow on the surface of the coal during the electrooxidation, which could have caused agglomeration of the coal particles. Pt with loading of 5.1 mg cm⁻¹ and Pt–Rh with loading of 1.7 mg cm⁻¹ carbon fiber bundle were influenced by flowing slurries of coal and graphite and showed the negative effect of erosion. These electrodes lost valuable coating of noble metals due to this erosive effect. Rh seems to have a very good adherence with carbon fibers since Rh coating was not observed to worn off due to erosion. Finally, the energy consumption for the production of hydrogen was found to be almost same for all the electrode materials tested. The energy consumption was about 22 Wh g⁻¹ of H₂, which is 50 % lower than that for hydrogen production by electrolysis of water under similar operating conditions (tem-

perature and current density). This fact demonstrates that coal electrolysis is a competitive method for in situ hydrogen generation.

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References

- [1] R.W. Coughlin, M. Farooque, *Nature* 279 (1979) 301–303.
- [2] P. Patil, Y. De Abreu, G. G. Botte, *J. Power Sources*, (in press).
- [3] M. Farooque, R.W. Coughlin, *Fuel* 58 (1979) 705–712.
- [4] R.W. Coughlin, *Ind. Eng. Chem. Prod. R.D.* 8 (1969) 12–23.
- [5] R.W. Coughlin, M. Farooque, *Ind. Eng. Chem. Process Des. Dev.* 21 (1982) 559–564.
- [6] M. Farooque, R.W. Coughlin, *Nature* 280 (1979) 666–668.
- [7] G. Okada, V. Guruswamy, J.O'M. Bockris, *J. Electrochem. Soc.* 128 (1981) 2097–2102.
- [8] O.J. Murphy, J.O'M. Bockris, *Int. J. Hydrogen Economy* 10 (1985) 453–474.
- [9] R.P. Baldwin, K.F. Jones, J.T. Joseph, J.L. Wong, *Fuel* 60 (1981) 739–743.
- [10] P.M. Dhooge, D.E. Stilwell, S.M. Park, *J. Electrochem. Soc.* 129 (1981) 1719–1724.
- [11] P.M. Dhooge, S.M. Park, *J. Electrochem. Soc.* 130 (1983) 1029–1036.
- [12] P.M. Dhooge, S.M. Park, *J. Electrochem. Soc.* 130 (1983) 1539–1542.
- [13] S.B. Lalvani, R.W. Coughlin, *Fuel Process. Technol.* 11 (1985) 37–46.
- [14] G.G. Botte, "Electrocatalysts and Additives for the Oxidation of Solid Fuels and their Application to Hydrogen Production, Fuel Cells, and Water Remediation Processes", Pending Patent, US, 2005.
- [15] R.H. Lochner, J.E. Matar, *Designing for Quality*, Productivity Press, Portland, 1990, p. 25.