

Feasibility of hydrogen production from coal electrolysis at intermediate temperatures

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Abstract

Hydrogen production via coal electrolysis was evaluated at intermediate temperatures (40–108 °C). A coal electrolytic cell (CEC) was designed and constructed to carry out galvanostatic experiments with concentrated electrolyte (4 M H₂SO₄). Operating temperatures above 100 °C were found to significantly improve the kinetics of electro-oxidation of coal, coal conversion, and CO₂/coal Faradaic efficiency. CO₂/coal Faradaic efficiencies and coal conversions of up to 57.29 and 3.21%, respectively, were observed at 108 °C.

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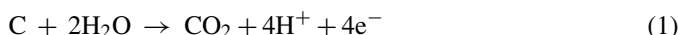
Keywords: Coal electrolysis; Hydrogen production; Coal gasification; Coal conversion; Coal utilization; Coal electrolytic cell

1. Introduction

In many ways, hydrogen is an excellent fuel source since it can be combined with air/oxygen in fuel cells to produce electricity cleanly and efficiently. Generally, hydrogen is produced from water electrolysis, natural gas, or coal gasification. However, each of these methods has disadvantages; natural gas has limited supplies worldwide and water electrolysis acquires significantly high power, so coal is an attractive source for hydrogen production.

Coal gasification has been used extensively in the past as an inexpensive method of hydrogen production via gasification. However, this method requires high temperatures (above 800 °C) and has associated with high costs of separating gaseous products and dealing with pollutants, such as SO_x and NO_x. An ideal method of hydrogen production from coal would eliminate these costs while operating at significantly lower temperatures. The electrolysis of coal is a technology that can realize many improvements over-gasification; environmental advantages of this process and economics analysis have been discussed in previous studies [1,2]. Electrolysis of coal was first proposed 25 years ago by Coughlin and Farooque [3–7]. According to the authors [3], coal is oxidized at the anode of the electrochemical

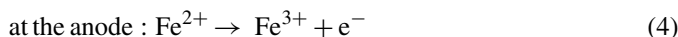
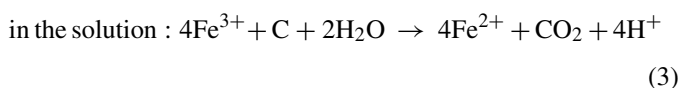
cell according to the following reaction:



while protons are reduced to produce hydrogen at the cathode:



The theoretical standard potential for this process is 0.21 V, which is significantly lower than the standard potential of water electrolysis (1.23 V). In their experiments, Coughlin and Farooque [3–7] found that the electrolysis of coal requires a cell potential in the range of 0.7–0.9 V, which is higher than the theoretical potential. Additionally, the authors indicated that the iron ions released from the coal play a part in the oxidation process. Indeed, later studies [8–13] showed that the current of coal electrolysis was mainly attributed to Fe(II) ions leached into the solution from the carbonaceous material. Several researchers [8–10,12,14–16] have hypothesized that Fe(II) is oxidized at the anode to Fe(III), which in turn mediates the oxidation of coal; this process can be represented by the reactions shown in Eqs. (3)–(5):



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at the cathode:



Eqs. (3)–(5) only describe the reduction of Fe(III) in solution and do not consider the electro-oxidation of coal on the anode. However, Patil et al. [1] observed that the coal oxidation process was enhanced electrochemically by Fe(II)/Fe(III) and proposed a modified mechanism, namely that the contact of coal particles with the surface of the anode increased the reaction rate of reduction of Fe(III) to Fe(II), thus enhanced the electro-oxidation of coal. Therefore, Patil et al. [1] proposed that Eq. (3) is enhanced by the contact of coal particles with the anode because (1) the concentration of Fe(III) is higher at the electrode surface than at the bulk, (2) the reduction of Fe(III) could be enhanced by compounds that are dissolved or leached from the coal surface, and (3) this process may be speeded by the mechanical abrasion that takes place during coal/electrode collisions.

The standard potential of the electro-oxidation of Fe(II) to Fe(III) is 0.77 V versus SHE. Although the reactions shown in Eqs. (3)–(5) do not take place at a cell potential comparable with the reactions described by Eqs. (1) and (2), the electrolysis of coal with additional iron ions has the following advantages: (1) including the high over-potential of water electrolysis, oxidation of Fe(II) at the anodic side occurs at a 50% lower potential than oxygen evolution, (2) Fe(II) can be regenerated by the oxidation of coal, realizing a sustained hydrogen production, (3) the gaseous products of the electrolysis do not contain pollutants such as NO_x and SO_x, (4) the electrolysis process takes place at lower temperatures than coal gasification.

Though coal electrolysis seems to be a promising method to produce hydrogen, the current densities observed by researchers in the 1970s and 1980s were prohibitively low. Recently, other researchers have made a significant progress to overcome this limitation [1,2]. Patil et al. [1] determined that electrodes containing Pt–Ir show the most promise as anodes for coal electrolysis based on operating cell voltage, and also observed the synergistic effect of the presence of Fe(II)/Fe(III) in solutions during the electrolysis. Both findings led to increased sustainable current densities within the electrolysis cell.

Sathe and Botte [2] evaluated the electrolysis of coal on carbon fiber electrodes plated with different combinations of the noble metals Pt, Ir, and Rh. A factorial experimental design was used to determine the most promising electrode composition and loading based on CO₂ Faradaic efficiency (that is, to maximize the oxidation of coal to CO₂). The authors also investigated the electro-oxidation of high purity graphite and compared the results with those observed for Pittsburgh No. 8 coal. The authors reported the following significant findings [2]: (1) Pt and Pt–Ir at loadings of 5 mg cm⁻¹ on a carbon fiber bundle as cathode and anode, respectively, provided the highest CO₂ Faradaic efficiency among tested compositions, (2) as the anode, erosion effects (due to the contact of the coal with the electrode) are lowest on Pt–Ir electrodes with similar loadings, (3) the CO₂ Faradaic efficiency is increased by the presence of graphite in the slurry. The authors proposed two reasons for the effect: (1) graphite acts as a dispersant for coal particles, and

(2) the graphite helps removing some of the films that grow on the surface of the coal during oxidation that inhibit the complete oxidation of coal to CO₂, and (4) the energy consumption for the production of hydrogen was 22 Wh g⁻¹ or 50% lower than the electrolysis of water at the same operating conditions.

De Abreu et al. [17] performed characterization of coal slurries after electrochemical oxidation. The authors found that in addition to increasing the CO₂ Faradaic efficiency of the process, increasing temperature up to 80 °C also changes the composition of the films found on the surface of the coal.

Based on the results reported by Sathe and Botte [2] and De Abreu et al. [17], the conversion of coal to CO₂ can be enhanced by increasing electrolysis temperature. Within this context, the objective of this paper is to evaluate the feasibility of coal electrolysis at intermediate temperatures (40–108 °C) for hydrogen production. Polarization techniques were used to achieve the objective. The experiments were performed in a continuous coal electrolytic cell (CEC), which was specially designed to operate at intermediate temperatures; the design was based on the low temperature continuous coal electrolytic cell described by Sathe and Botte [2].

2. Experimental set-up

2.1. Preparation of electrodes

Based on the findings reported by Sathe and Botte [2], Pt–Ir and Pt on BASF Polyacrylonitrile (PAN) carbon fiber substrates (from Celion G30-500, 7 μm diameter) were used for the anode and cathode of CEC, respectively. The electrodes were prepared using the procedures previously described by Sathe and Botte [2], while several changes were made for the electrode design based on the operating conditions of the coal electrolytic cell. In order to operate the coal electrolytic cell at temperatures between 100 and 160 °C at 1 atm pressures, high concentrations of sulfuric acid electrolyte were needed, which necessitated the use of Hastelloy which can tolerate the operating temperature and high concentration of sulfuric acid as a current collector. However, Hastelloy has higher electronic resistance (1.3 μΩ m [18]) than the titanium current collector used by Sathe and Botte (0.420 μΩ m [2]). Therefore, the conditions of the plating bath were modified accordingly (salt concentration was increased) realizing a plating current of 50–80 mA at a plating potential of 1.1 V. Table 1 shows a summary of the plating conditions used for preparation of the electrodes. The plating salts (99.9% purity obtained from Alfa Aesar) and instrumentation used for electro-deposition are the same as described by Sathe and Botte [2].

The electrodes were made in circular shape, so they could be used in a cylindrical CEC designed with the intention of improving the flow of the slurry through the cell. Fig. 1 shows the schematic procedure for the preparation of the electrodes. Each circular Hastelloy gauze (metal gauze 20 mesh gauze woven of 0.23 mm diameter wire from Alfa Aesar) had a diameter of 2 cm. A Hastelloy wire (0.51 mm diameter, 12 cm long wire from ESPI metals) was attached to the gauze. The carbon fiber bundle was wrapped to the gauze and the ends of the carbon fibers and the

Table 1
Experimental parameters for plating of Pt and Pt–Ir on the carbon fiber electrodes with Hastelloy gauze as supporting current collector

Parameters\electrodes	Pt	Pt–Ir
Salt	H ₂ PtCl ₆ ·6H ₂ O	H ₂ PtCl ₆ ·6H ₂ O + IrCl ₃
Solutions	1 M HCl prepared with ultra high purity water	1 M HCl prepared with ultra high purity water
Concentration of salt (mg ml ⁻¹)	6.3 (H ₂ PtCl ₆ ·6H ₂ O)	1.7 (H ₂ PtCl ₆ ·6H ₂ O) 3.0 (IrCl ₃)
Temperature of plating bath (°C)	80	80
Current (mA)	50–100	80–120
Cell voltage range (V)	1.1–1.2	1.1–1.2
Plating time (h)	5.2	6.8
Counter electrode	Pt electrode foil (2 × 4 cm). Purity: 99.95% from Electronic Space Products International (ESPI) Company	

Hastelloy wire were held together by a Hastelloy clip (made of 4 mm × 6 mm, 0.1 mm thickness foil from ESPI Metals). The prepared electrodes were cleaned with acetone to remove any grease or dirt and were weighted before and after plating. The resulting electrodes contained a bundle of carbon fibers (6000 fibers per bundle) 39.2 cm long for cathode and 36.8 cm long for anode. The total loading (Pt–Ir) of the anode was 5.3 mg cm⁻¹ and the total loading (Pt) of the cathode was 6.0 mg/cm of carbon fiber bundle.

2.2. Construction of intermediate temperature coal electrolytic cell (CEC)

The design of the CEC was made in conjunction with the Edison Materials Technology Center (EMTEC). Fig. 2a shows the structural design of one chamber of the CEC. The cell was manufactured in a circular/cylindrical shape to enhance the flow of the slurry through the electrode and to minimize the ohmic resistance caused by accumulation of coal on the electrodes. The

cell consisted of two identical symmetrical chambers, one for the anode, and one for the cathode. An O-ring was placed between the two chambers to seal the cell and four screws were used to assemble the cell. Fig. 2a shows the anodic compartment of the cell where: “a” and “b” are the outlet and inlet for the anodic solution, respectively; “c” is the opening for the thermocouple (only one thermocouple was inserted in the cell and it was placed on the anodic compartment); and “d” is the opening for the electrode current collector wire. The dimensions of the fittings used are given in Fig. 2a. The cathodic compartment of the cell was identical with the anodic one, except that no fitting was included for a thermocouple.

Fig. 2b shows a picture of the two compartments of the CEC. The cell was made with Teflon rods (Virgin Electrical Grade Teflon rod with 76.2 mm diameter from McMaster–Carr) which can withstand the operating temperature and electrolyte media in the cell. The O-ring seal was made of Kalrez (purchased from Ace Glass). PFA (Perfluoroalkoxy, which has excellent chemical resistance to H₂SO₄, obtained from McMaster–Carr) compression fittings were used for inlets, outlets, thermocouples, and electrodes’ current collectors. A proprietary polyethylene membrane was used as a separator for the anode and cathode.

Fig. 2c shows a picture of the CEC, which is assembled and connected to the pump, reservoir and potentiostat with the compression fittings. The solution enters through the center of the cell (coming directly from the reservoirs, see Fig. 3), and leaves the compartment through the side outlet (which is placed on the side just after the electrode, see Fig. 2a). The tubing from the side outlets are connected to pumps which transport the solution back to the reservoirs (see Fig. 3). The electrode current collector wire, which comes from the inner side through the Teflon coating septum (purchased from Ace glass) was connected to the potentiostat (Arbin or Solartron). A Teflon coated J-type thermocouple (12140-20 from Ace Glass) connected with a heating tape and a temperature controller was used to measure and control the temperature of the CEC.

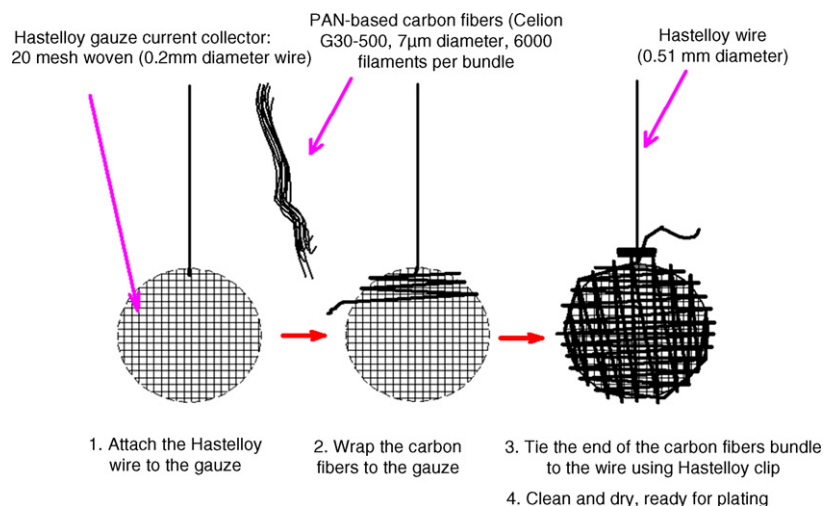


Fig. 1. Schematic representation of the procedure used for the preparation of the carbon fiber electrodes. Hastelloy gauze and Hastelloy wire were used for the frame and current collector of the electrodes, respectively. Carbon fibers were wrapped around the gauze.

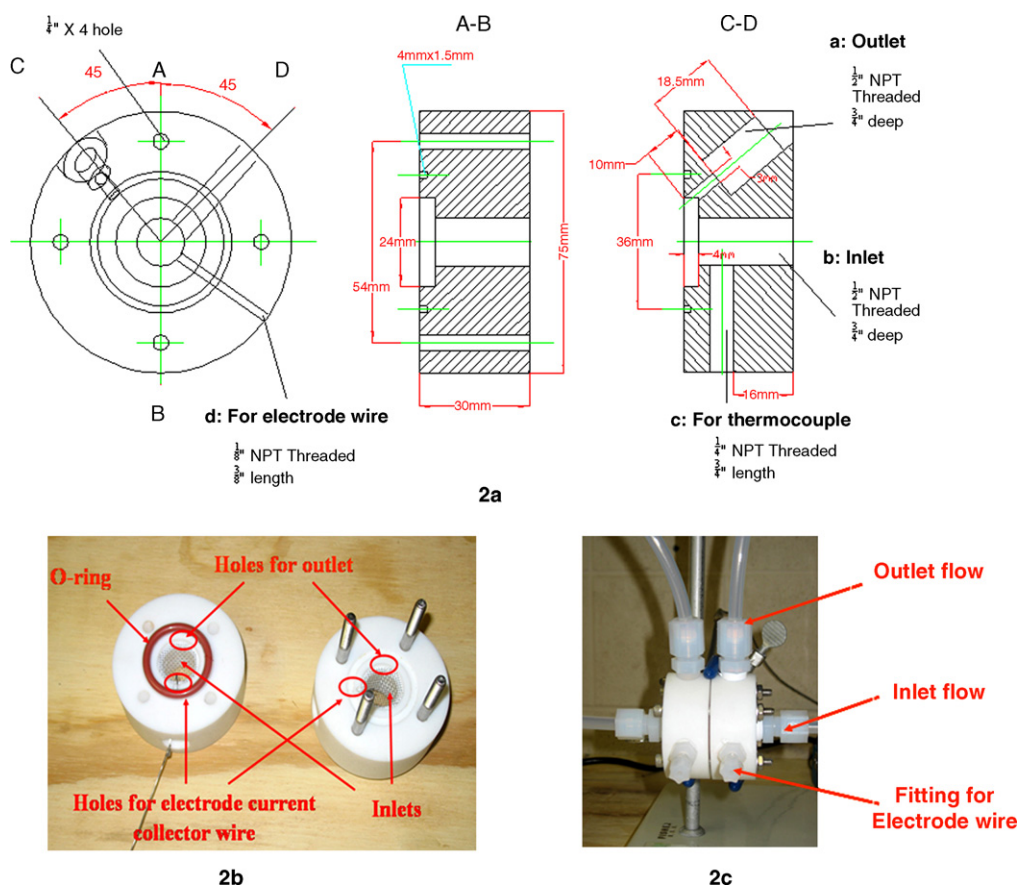


Fig. 2. Coal electrolytic cell (CEC) for intermediate temperatures. 2a: Different views of the cell. “a” is the outlet opening, “b” is the inlet opening, “c” is the opening for the thermocouple, and “d” is the opening for the electrode. 2b: Photograph of the internal parts of the cell. Teflon rod was used for the main body of the cell and an O-ring was used to seal. 2c: Photograph of cell assembled and connected to the tubing of the testing system. Two electrodes were connected to the Arbin or Solartron system, inlets were connected to the anodic and cathodic flasks using the Teflon fittings, outlets were connected to the pumps using the Teflon tube and fittings, and the thermocouple was connected to the temperature controller.

The advantages of this cell design are excellent sealing, ease of assembly and disassembly, short distance between the electrodes, and enhancement of the contact of the reactants with the electrodes (the solutions travel around the circular/tubular chamber where the electrodes are located, increasing the resident time of the solution with the electrodes).

2.3. Intermediate temperature CEC set-up

Fig. 3 shows a schematic diagram of the intermediate temperature CEC bench-scale testing system, which was designed to operate at temperatures no higher than 160 °C. Galvanostatic experiments were carried out by an Arbin (BT2000) and/or a Solartron system (S1 1287 electrochemical interface). The capacities of the anodic and cathodic reservoirs are 500 ml. Instatherm heating coating (made by Ace Glass) on the body of the reservoirs, together with the thermocouples and temperature controllers (same as described as in Section 2.2), was used to control the temperatures of anodic and cathodic solutions. Teflon PFA tubing (51805K73) from McMaster–Carr was used to transport the anodic and cathodic solutions, which were circulated in and out of the cell with the help of QG gear pumps (the pumps have ceramic and Teflon heads to withstand concentrated sul-

furic acid electrolyte and the operating temperature, purchased from Fluid Metering Inc.) at an average flow rate of 65 ml min⁻¹ to guarantee sufficient contact between the solutions and the electrodes. The solutions were stirred with the help of Fisher Scientific Thermix Magnetic stirrers (model 220T). Condensers were added to the system to keep the level of solution in the reservoir constant; the temperature of the cooling water was kept at 20–25 °C. Gas products were collected in measuring cylinders by the method of displacement of water.

In comparison with the set-up used by Sathe and Botte [2], this testing system has several advantages: (1) compression fittings, O-ring, and PFA tubing ensure a better sealing condition; (2) the materials of the pump, tubing, fittings, and the cell can withstand operation temperature up to 160 °C. Appropriate membranes and electrolytes can make the continuous setup to perform coal electrolysis experiments above 120 °C and (3) flow direction can easily be changed.

3. Experimental conditions and methodology

Galvanostatic experiments were carried out to test the feasibility of the coal electrolysis at intermediate temperatures. Concentrated sulfuric acid (4 M) was used as the electrolyte and

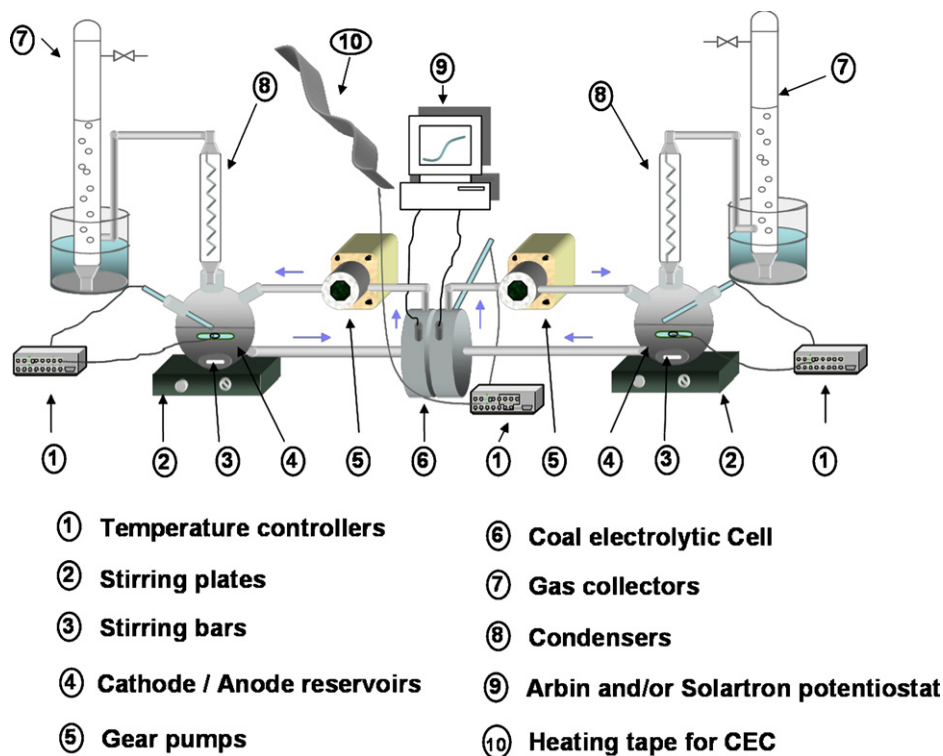


Fig. 3. Schematic of the continuous bench-scale testing system for coal electrolysis at intermediate temperatures. Magnetic stirring plates and stir bars were used for stirring the solutions, reservoirs contain the anodic and cathodic solution, cell is the vessel for the electrolysis reaction, pumps were used to circulate the solution. Temperature controller, thermocouple, Instatherm coating (on the reservoirs), and heating tapes were used to control the temperature of the cell and reservoirs. Condensers were used to condense the vapor and gas collectors were used to collect the hydrogen and carbon dioxide product gases.

reagent grade crystal $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ (from Fisher Scientific) were added to the anodic solution to increase the operating current of the cell as suggested by Patil et al. [1]. Pittsburgh No. 8 coal (particle size 74–105 μm from Penn State Coal Bank: Sample DECS-12) was used for the anodic solution. Coal and graphite samples were stored as recommended in the literature [2]. The volume of anodic and cathodic solutions was 300 ml.

In order to study the effect of iron on the electro-oxidation of coal and determine the efficiency of coal conversion, experiments were carried out with two different anodic solutions (blank and coal/iron solutions). The blank experiment was performed with a solution of 100 mM Fe(II)/100 mM Fe(III) and electrolyte; this experiment served as a reference to determine the Faradaic efficiency of the coal electro-oxidation. In the coal/iron experiments, the concentration of coal was kept at 0.02 g ml^{-1} along with 100 mM Fe(II)/100 mM Fe(III). Galvanostatic experiments were performed at 0.1 A; experiments were stopped if the cell voltage reached 1.2 V in the interest of avoiding water electrolysis.

The concentrations of Fe(II) and Fe(III) in solution were measured using the rotating disk polarization method [19]. This method allows simultaneous measurement of the concentrations of Fe(II) and Fe(III) based on the ions' limiting currents. More information on the technique is provided in the literature [19].

In all cases, the experimental error was calculated by propagation of error based on the experimental uncertainties of the instrumentation and/or equipment.

4. Results and discussion

4.1. Concentration of iron during the electrolysis of coal

Galvanostatic tests were carried out with coal/iron slurry solution and blank solution (experimental conditions were described in Section 3) separately at 80°C on the setup shown in Fig. 3. The polarization results of the experiments are shown in Fig. 4. As indicated in Fig. 4, the testing time for the coal/iron

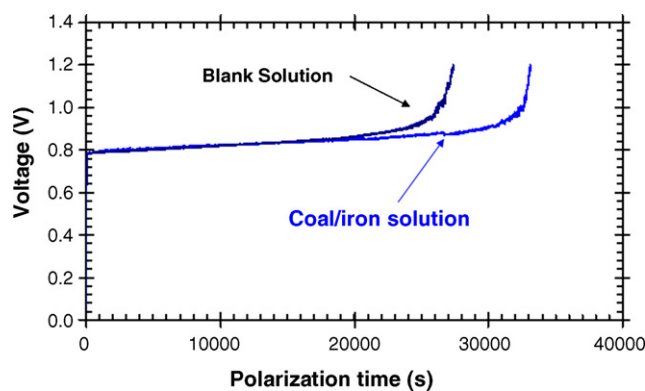


Fig. 4. Galvanostatic (0.1 A) results for coal and blank solutions at 80°C (4 M H_2SO_4 as the electrolyte, 100 mM Fe(II)/100 mM Fe(III), and 0.02 g ml^{-1} coal). Coal electrolysis trials lasted longer than the electrolysis of the blank solution, which can be attributed to oxidation of coal by Fe(III) according to coal chemical oxidation Eq. (3), direct coal electro-oxidation Eq. (1), and/or a combination of Reactions (3) and (4).

Table 2

Concentration of iron ions before and after electrolysis reactions on the CEC at 80, 100 and 108 °C according to the conditions described in Figs. 4, 6 and 8, respectively

Experiment/section	Fe(II) before ± 4 mM	Fe(III) before ± 2 mM	Fe(II) after ± 2 mM	Fe(III) after ± 14 mM	Fe(II) mM Faraday's law ± 4 mM	Fe(III) mM Faraday's law ± 4 mM
80 °C, coal/iron	97	101	6	200	−17	216
80 °C, blank solution	98	101	6	197	4	196
100 °C, coal/iron	98	101	5	201	−43	241
100 °C, blank solution	98	101	1	199	−1	200
108 °C, coal/iron	99	101	4	198	−136	336
108 °C, blank solution	99	101	0	201	−2	202

The concentration of iron ions in solution was measured using the method described by Botte and Jin [19].

solution was 33,118 s, while the testing time for the blank solution was 27,372 s. The concentrations of Fe(II) and Fe(III) were measured before and after the electrolysis; results are reported in Table 2.

The results showed that most of the Fe(II) was oxidized to Fe(III) during the polarization tests. For the blank solution, a small concentration of Fe(II) (6 ± 2 mM) was left in the solution while the Fe(III) concentration (197 ± 14 mM) was almost equal to the total concentration of original Fe(II) and Fe(III), which agrees with the results calculated from Faraday's law (based on the operating time of the cell and applied current). It is also shown in Fig. 4 that the required cell potential for iron oxidation is 0.78 V at initial concentrations, which is consistent with the standard potential of Fe(II) oxidation, and proves that the over-potential for Fe(II) electro-oxidation reaction is small. The concentrations of Fe(II) and Fe(III) were calculated for the coal/iron solution by using Faraday's law and assuming that only Eq. (4) takes place and the results are shown in Table 2. If only Eq. (4) takes place, the system should have run out of Fe(II) ions (as described by the negative values shown in Table 2), while the concentration of Fe(III) should be higher than that measured experimentally. Based on these findings, there are three possible explanations for the difference in the reaction time obtained between the blank solution and the coal/iron solution: (1) electrochemical reactions described by Eqs. (1) and (4) take place simultaneously at the surface of the anode; (2) Fe(II) is oxidized at the anode according to Eq. (4), while Fe(III) is reduced to Fe(II) at the surface of the coal according to Eq. (3) (since Eq. (3) is a chemical reaction, contact with electrode surface may not be necessary) and (3) a combination of both 1 and 2.

In this paper, the CO₂/coal electro-oxidation efficiency and coal conversion were calculated using the following equations:

$$\eta_{\text{CO}_2} = \frac{t_{\text{total}} - t_{\text{iron}}}{t_{\text{total}}} \quad (6)$$

$$\eta_{\text{Coal}} = \frac{m_{\text{reaction}}}{m_{\text{total}}} \quad (7)$$

where η_{CO_2} is the CO₂/coal electro-oxidation Faradaic efficiency, t_{total} the total polarization time of the coal slurry solution, t_{iron} the polarization time of the blank solution, η_{Coal} the coal conversion efficiency, m_{reaction} the mass of the coal which was oxidized (calculated from η_{CO_2}) and m_{total} the initial mass of coal in the reservoir flask. One advantage of this calculation

method is the low experimental uncertainty. Experimental error in these measurements is due to the uncertainties in polarization time (± 1 s) and weight (± 0.0001 g) measurements. Therefore, if experimental error is calculated using propagation of errors, the maximum uncertainties will be less than 0.01% for both the Faradaic efficiency and coal conversion efficiency. Consequently, values for these variables are reported with two decimal.

Using Eq. (6), the CO₂/coal electro-oxidation Faradaic efficiency at 80 °C is 17.29%, (82.71% of the current contributed to the electro-oxidation of Fe(II)), but the coal conversion is only 0.30%. Possible explanations for the low coal conversion are: (1) the kinetics of chemical oxidation and/or electro-oxidation of coal is much slower than Fe(II) electro-oxidation, and (2) films formed on the surface of the coal particles [17] stop the further oxidation of coal. In order to increase the CO₂/coal Faradaic's efficiency and coal conversion, the temperature needs to be increased; this should enhance coal oxidation according to Eq. (3) and electro-oxidation of coal according to Eq. (1), as well as minimize the formation of films on the surface of the coal particles during electrolysis [17].

It is important to discuss the validity of Eq. (6) for the estimation of the CO₂ Faradaic efficiency. During experiments, the concentration of the gaseous products changed dramatically, which made it inappropriate to calculate CO₂ efficiency by utilizing the gas collected and assuming constant concentration of CO₂; it was also found that the pump transports air into the system during the circulation process. Therefore, in order to calculate the CO₂ Faradaic efficiency based on collected gas volume, the gas volume needs to be corrected by the concentration of CO₂ measured in the mixture of gases as described by Sathe and Botte [2]. This method is tedious and time consuming, as all the samples collected must be analyzed using a gas chromatograph. In this study, Eq. (6) was used, which is easier and faster. The validity of Eq. (6) was tested by comparing with the results reported by Sathe and Botte [2]. For example, at 80 °C, the predicted CO₂ Faradaic efficiency based on Eq. (6) is 17.29%, while Sathe and Botte reported 18.00% for the same operating conditions; this agreement was deemed valid for our objective. However, the reported values are described as CO₂/coal Faradaic efficiency because part of the coal could have been electro-oxidized to form films on the surface of the coal particles with no release of CO₂.

Before increasing the temperature in the CEC, experiments were performed to distinguish chemical coal oxidation Eq. (3)

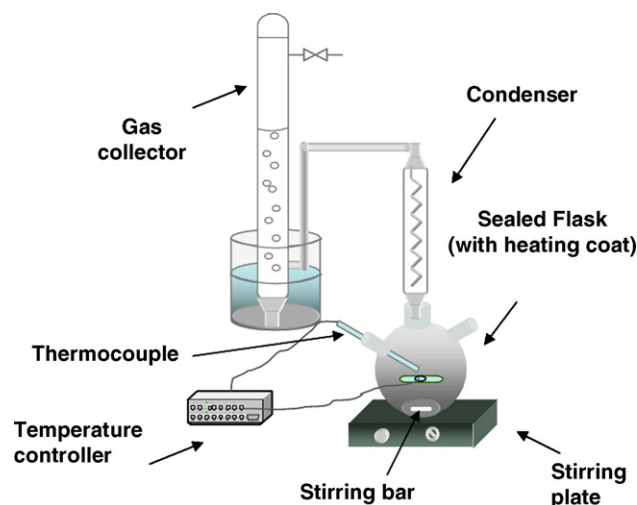


Fig. 5. Schematic of the setup used for the investigation of coal chemical oxidation in the presence of Fe(III). A magnetic stirring plate and stir bar were used for stirring the solution. Temperature controller, thermocouple, and Instatherm coating were used to control the temperature of the flask. A condenser was used to condense the vapor before the gas collector.

and electrochemical coal oxidation [1]. These results are discussed in Section 4.2.

4.2. Coal chemical and electrochemical oxidation

Coal can be chemically oxidized by Fe(III) into CO_2 during the electrochemical oxidation of coal since Fe(III) ions are present in solution. Therefore, in order to distinguish the two processes, it is necessary to get a better understanding of the chemical oxidation of coal. Experiments at different temperatures were carried out in a sealed flask system as shown in Fig. 5. During the experiments, the gaseous products were collected and the concentrations of iron ions were measured. The results of the chemical oxidation of coal at 40, 80, 100, and 108 °C are summarized in Table 3. In all experiments, gases were collected for 20 min; after this time, there was no significant change in the volume of the gas and in the concentration of iron ions. According to the stoichiometry shown in Eq. (3), the volume of gas liberated was calculated theoretically by using the change in the concentration of Fe(III) measured before and after the experiment. Considering the error of the experimental instruments and iron ion measurement, these theoretical values of the gases volume are in acceptable agreement with the gas volume collected.

Table 3
Efficiency of the chemical conversion of coal to CO_2 during chemical oxidation in the presence of Fe(III) at different temperatures

T (°C)	Fe(II) mM before	Fe(III) mM before	Fe(II) mM after	Fe(III) mM after	Gas volume measured (ml)	Gas volume calculated (ml)	η_{coal} (%)
40	97 ± 4	100 ± 2	100 ± 4	99 ± 2	5 ± 1	5 ± 5	0.05 ± 0.01
80	98 ± 4	102 ± 3	105 ± 4	94 ± 2	15 ± 1	13 ± 5	0.12 ± 0.01
100	98 ± 4	101 ± 2	112 ± 4	90 ± 1	36 ± 1	25 ± 5	0.22 ± 0.01
100	98 ± 4	205 ± 14	111 ± 4	219 ± 15	35 ± 1	24 ± 5	0.22 ± 0.01
108	97 ± 4	100 ± 14	115 ± 4	85 ± 1	41 ± 1	32 ± 5	0.29 ± 0.01

The conversion of coal to CO_2 increases with increasing temperature.

Results in Table 3 show that more gas was produced when increasing the temperature; that is, increasing temperature favors the chemical oxidation of coal by Fe(III). The effect of higher concentrations of Fe(III) (200 mM) on the chemical oxidation of coal at 100 °C was also tested. The volume of collected gas does not change as compared with the solution with 100 mM Fe(III), which indicates that the concentration of Fe(III) does not affect the chemical oxidation of coal. The coal conversion was also included in Table 3, the results show that the chemical conversion of coal is at the same magnitude as the electro-oxidation conversion at low temperatures (below 80 °C), but it is much lower at intermediate temperatures (above 80 °C, see Section 4.5).

Sathe and Botte [2] showed that when carbon fibers alone were used as anode, coal was not oxidized to CO_2 . According to their results, the noble metals plated on the electrodes are necessary for the electro-oxidation of coal, and the mechanism is completely different from chemical oxidation. Results from this study further confirm the findings of the authors [2]. Patil et al. [1] proposed a mechanism for the electrolysis of coal, but they did not distinguish between the coal chemical oxidation and coal electro-oxidation, nor did their mechanism consider the steps that limit the reaction. In addition, the effect of potential on the reaction also needs to be determined. Additional studies of the coal electro-oxidation at the surface of the noble metal catalyst are important to determine the mechanism of coal electrolysis, which will help to improve coal conversion efficiency. Results on this topic will be presented in future studies.

4.3. Temperature effect on Fe(II) electro-oxidation

As shown in Section 4.1 the current collected from galvanostatic experiments was mostly due to the electro-oxidation of Fe(II). Therefore, in order to increase the Faradaic efficiency for the electro-oxidation of coal, it is necessary to analyze the factors affecting the electro-oxidation of Fe(II) to Fe(III). Fig. 6 shows the effect of temperature on the electro-oxidation of Fe(II) at the same operating conditions described in Section 4.1 (here only blank solution was used). The results show that increasing the temperature did not decrease the cell voltage required for this process, but did increase the conversion of iron ions from Fe(II) to Fe(III). However, at above 100 °C, there is no change in polarization time, which indicates that temperatures higher than 100 °C do not affect the electro-oxidation of Fe(II). The increased conversion of Fe(II) to Fe(III) observed from 80 °C to 100 °C is likely due to the increase diffusion of ions caused

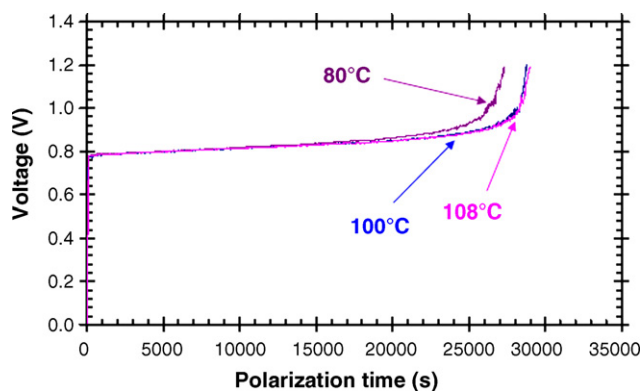


Fig. 6. Effect of intermediate temperatures (80, 100, and 108 °C) on the electro-oxidation of iron (II). Experiments were performed with 4 M H₂SO₄ as electrolyte, 100 mM Fe(II) and Fe(III), and an applied current 0.1 A. The maximum conversion of Fe(II) is achieved at 100 °C on the described experimental setup.

by the increase of the temperature. The change in concentration of Fe(II) and Fe(III) at different temperatures are shown in Table 2. These results indicate that the polarization time at temperatures of 100 °C and above match that predicted by Faraday's law for complete conversion of Fe(II), which means the maximum conversion of Fe(II) to Fe(III) is achieved when the temperature went up to 100 °C. The slightly negative values for the Fe(II) concentrations reported in Table 2 according to Faraday's law are in agreement with the experimental uncertainty in the measurement of the concentrations of iron ions.

According to the Nernst equation, the ratio of the concentrations of Fe(II) and Fe(III) will also affect the cell potential. In order to study the effect of this concentration ratio on the cell potential, two experiments were carried out at 80 °C. One experiment was performed with the blank solution, which contained 100 mM Fe(II) and 100 mM Fe(III), while the other utilized a blank solution containing 100 mM Fe(II) only. Results from these experiments are shown in Fig. 7; these results indicate that the ratio of the concentration of Fe(II) and Fe(III) does not significantly affect the cell potential, a small effect is observed at short

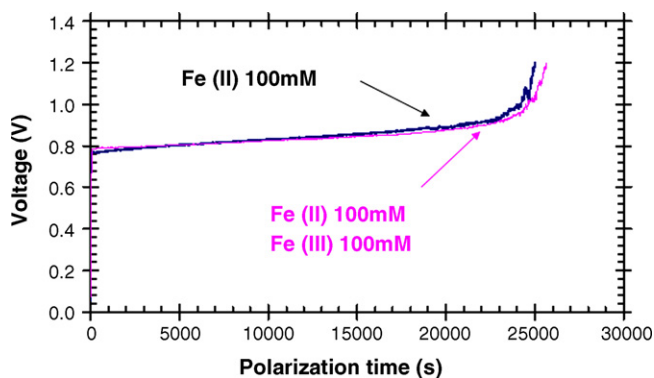


Fig. 7. Effect of the ratio of the concentrations of Fe(II) and Fe(III) on the cell potential during the electro-oxidation of iron. 4 M H₂SO₄ was used as electrolyte. The experiments were performed at 80 °C with a constant applied current (0.1 A). One blank solution contains 100 mM Fe(II) and 100 mM Fe(III), while the other solution only contains 100 mM Fe(II). Concentration ratio affects the cell potential a little at short times, but it does not affect the cell potential after several minutes.

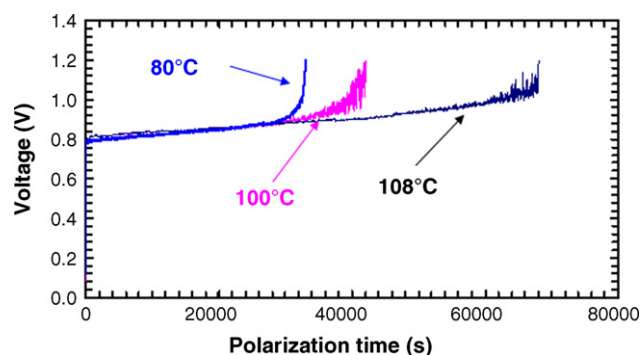


Fig. 8. Effect of intermediate temperatures (80, 100 and 108 °C) on the coal electrolysis. Experiments were performed with 4 M H₂SO₄ as electrolyte, 100 mM Fe(II) and Fe(III), 0.02 g mL⁻¹ coal, and applied current 0.1 A. Increasing temperature significantly increases the polarization time in the cell.

times (initial polarization potential), but the effect disappears after a few polarization seconds.

4.4. Temperature effect on coal electro-oxidation

Fig. 8 shows the results of the polarization experiments of coal slurries in the presence of Fe(II) and Fe(III) at different temperatures (80, 100, and 108 °C). Temperatures above 108 °C were not attempted as 108 °C is the flash point (at 1 atm) for 4 M sulfuric acid in water. The results indicate that the temperature significantly affects the electrolysis of coal; higher temperatures result in longer polarization times, which means that more coal is electro-oxidized. A dramatic effect is observed when the temperature is set at 108 °C; at this temperature, the polarization time was almost twice as long as that at 100 °C. Based on the results reported in Table 2, above 100 °C all Fe(II) is oxidized to Fe(III), therefore, most of the current observed is due to the electro-oxidation of coal.

4.5. Temperature effect on the CO₂/coal electro-oxidation efficiency and coal conversion

Fig. 9 and Table 4 show the effect of temperature on the CO₂/coal electro-oxidation Faradaic efficiency and coal conver-

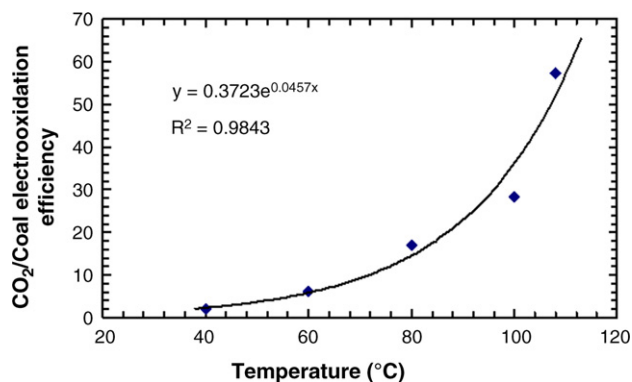


Fig. 9. Effect of temperature on CO₂/coal electro-oxidation Faradaic efficiency. Increasing temperature increases the efficiency from 2.1% at 40 °C to 56.3% at 108 °C. The results indicate that the Faradaic efficiency increases exponentially with temperature.

Table 4
Temperature effect on CO₂/coal Faradaic efficiency and coal conversion

Solution	Time (± 1 s)				
	40 °C	60 °C	80 °C	100 °C	108 °C
Blank solution	16,620	17,580	27,372	28,794	29,030
Coal/iron	16,980	18,360	33,117	40,563	67,972
η_{CO_2} ($\pm 0.01\%$)	2.12	6.25	17.34	29.01	57.29
η_{Coal} ($\pm 0.01\%$)	0.02	0.04	0.30	0.61	3.21

sion efficiency. The results indicate that increased temperature increases the CO₂/coal electro-oxidation Faradaic efficiency from 2.12% at 40 °C to 57.29% at 108 °C. That is, the coal conversion increased dramatically from 0.02% at 40 °C to 3.21% at 108 °C. The results may be attributed to two reasons: (1) increasing the temperature improves the kinetics of coal electro-oxidation; and/or (2) some films formed on the surface of the particles are dissolved/not formed at higher temperatures. The experimental data was regressed by using the correlation shown in Fig. 9 with a statistically significant representation of the data. The CO₂/coal electro-oxidation Faradaic efficiency seems to follow an Arrhenius type of relationship with operating temperature of the CEC. The energy consumption for the production of hydrogen was about 22.0 W h g⁻¹, which is congruous with the value reported by Sathe and Botte [2]. Worth to mention is that the current density is 32 mA cm⁻², which is much higher than the value (25 mA cm⁻²) reported by Sathe and Botte [2].

5. Conclusions

The electrolysis of coal was evaluated at intermediate temperatures. The circular/cylindrical CEC cell was shown to have good performance toward the electrolysis of coal at intermediate temperatures. Increasing temperature improved the kinetics of the coal electro-oxidation reaction, which significantly increased the Faradaic efficiency (η_{CO_2}), from 2.12% at 40 °C to 57.29% at 108 °C and coal conversion (η_{coal}) from 0.2% at 40 °C to 3.2% at 108 °C. The energy consumption for the production of hydrogen was about 22.0 W h g⁻¹, which is 50% lower than the water electrolysis at the same operation conditions. Experimental studies indicate that both the electro-oxidation and chemical oxidation of coal may be involved during coal electrolysis, and they have

different reaction mechanisms. More detailed studies are needed to determine the mechanism of coal electro-oxidation in order to further increase the Faradaic efficiency and conversion of coal. Higher temperatures (above 120 °C) are proposed to have better performance for coal electrolysis.

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