Electrooxidation of coal slurries on different electrode materials

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Abstract

The electrochemical behavior of coal–water slurries was examined with various noble metal electrodes (i.e. Pt, Pt–Rh, Pt–Ru, Pt–Ir and plated Pt on Ti foil) using potentiostatic techniques. It was found that there was no significant difference in the performance of the electrodes in the electrooxidation of coal; except for Pt–Ir, which out performed the other electrode materials. The effect of adding iron(III) and iron(II) on the electrooxidation of coal was also tested. It was found that the presence of iron(III) and iron(II) in the coal slurry significantly increased the average current densities developed in the coal electrolytic cell. The electrolysis of pure graphite was tested and compared to the electrolysis of coal to determine if any components or impurities present in the coal affected the electrooxidation of coal. It was also found that the iridium content in the electrode affects the electrochemical performance of the coal. The maximum faradaic efficiency found for the electrooxidation of coal on a Pt–Ir (80:20) electrode was 24% for CO_2 generation with an energy consumption of $21\,W\,h\,g^{-1}$ of hydrogen produced.
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1. Introduction

1.1. Coal electrolysis and hydrogen production

Hydrogen is expected to be a primary energy source in the 21st century for electricity generation, fuel and other applications. It is an environmentally clean energy source since it generates no pollutants but produces water, which can be recycled to make more hydrogen. Hydrogen energy is becoming increasingly important as recent technology progress makes hydrogen a realistic energy option. However, hydrogen is not a primary source of energy since it does not exist in free forms on earth. Hydrogen can be found in water and several other chemical compounds from which it has to be separated before it can be used. Fossil fuels and water are the major sources for the manufacture of hydrogen. However, these processes are highly energy intensive and not always environment-friendly [1]. Moreover, the fossil fuel (mainly petroleum) reserves of the world are depleting, therefore, it has become extremely important to develop more efficient and less expensive methods of H_2 production based on the available energy sources.

Coal, which is considered the cheapest source of energy, has been used extensively in the past for the production of hydrogen by gasification (discussed elsewhere [2]), but this method requires a very high temperature (approximately 800 °C) and it also requires the purification of the gases. Coal gasification is most likely to be used in the large scale production of hydrogen, because of the high temperatures and the separation units required, but it may not be easy to implement for on-site production of hydrogen (e.g. distributed hydrogen units up to 1000 kg of hydrogen per day [3] and small portable units to power residential houses). In 1979, Coughlin and Farooque proposed a new method called electrochemical gasification of coal water slurries [4], which generates pure streams of CO_2 and hydrogen at the anode and cathode, respectively, free of tar and sulfur compounds, according to the following reactions:

$$4H^+ + 4e^- \rightarrow 2H_2 \tag{1}$$

$$C_{(s)} + 2H_2O_{(l)} \rightarrow CO_{2(g)} + 4H^+ + 4e^- \tag{2}$$
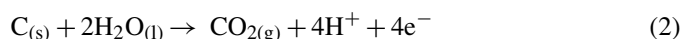
Reactions (1) and (2) take place at the cathode and anode of the coal electrolytic cell, respectively. The overall reaction is given by

$$C_{(s)} + 2H_2O_{(l)} \rightarrow CO_{2(g)} + 2H_{2(g)} \tag{3}$$
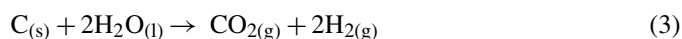
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Platinum electrodes were used in the electrochemical cell described [4]. The authors reported that the reversible thermodynamic potential of the cell at standard conditions (25 °C and 1 atm) is only 0.21 V. Therefore, thermodynamic values are much in favor of the production of hydrogen by the electrolysis of coal slurries than the electrolysis of water, for which the thermodynamic standard cell potential is 1.23 V. Because of the low temperatures of the reaction and the simplicity of the process (separation units are not required to produce clean hydrogen), the electrochemical gasification of coal slurries or coal electrolysis could find a potential market in distributed power and small hydrogen generators.

Other researchers have reported the effect of different parameters (coal particle size, coal concentration and temperature) on the electrooxidation of various kinds of coal (Pittsburgh coal, North Dakota lignite, activated charcoal and Montana Rosebud char) using Pt as anode [5–10]. Baldwin et al. studied the electrooxidation of coal using voltammetry techniques [11]. Other authors have evaluated the effect of coal concentration, pH and additives (Fe and Ce) on the electrooxidation of coal [4,6,7]. It has also been reported that coal deactivates with time during the electrolysis (causing an increased in the cell potential) due to the formation of films on the surface of the coal particles [4,6,7]. Murphy and Bockris characterized the organic products formed after the electrolysis of lignite, concluding that the anodic reaction produces a mixture of C_8–C_{18} hydrocarbons [10].

1.2. Objectives of the study

One of the problems associated with the electrolysis of coal slurries is low reaction rate, which makes it economically unfavorable. Within this context, the objectives of this paper focus on the improvement of the electrooxidation rate of coal. This paper has four objectives:

(1) Evaluate the performance of different electrode materials on the electrooxidation of coal. The intention is to identify the materials that have a significant positive effect on the current density during the electrolysis of coal. Farooque and Coughlin [5] tested the effect of two different electrode materials (Pt and graphite electrodes) on the electrooxidation of coal. The authors reported that there were not significant differences in the current densities measured using either of the electrodes [5]. Even though this finding was reported, we hypothesized that other noble electrodes may have a positive effect on the current density. For example, Pt–Ru may be an alternative good catalyst in case that CO groups are formed during the oxidation of coal. The following electrode materials were tested Pt, Pt–Rh, Pt–Ru, Pt–Ir and plated Pt on Ti foil.
(2) Compare the electrolysis of coal with the electrolysis of graphite in order to provide a better understanding of the electrooxidation of coal.
(3) Determine the effect of iron on the electrolysis of coal and graphite on the best suitable catalyst (found in step 1).
(4) Calculate the faradic efficiency for the electrooxidation of coal on the best suitable catalyst (found in step 1) and the

energy consumption of a bench-scale batch coal electrolytic cell for the production of hydrogen.

Polarization techniques were used to achieve the objectives.

2. Experimental

2.1. Electrode preparation

Different electrode material foils (Pt, Pt–Ru, Pt–Ir and Pt–Rh) obtained from Alfa Aesar were cut into a rectangular shape of known area (2.1, 3.78, 2.8 and 2.61 cm^2, respectively). The composition of the electrodes is shown in Table 1. The cut foils were soldered to a copper wire of suitable length on to the center of one of the edges of the rectangular foil. The soldered part and most of the length of the copper wire was coated with a polymer (PTFE) paint, which is stable at high temperatures (120 °C) and resistant to the coal–water slurry in which it was tested. This coating was done twice and heated for 15–20 min in an oven at 200 °C (to ensure uniform distribution of the coating and sintering of the polymer) and finally air dried.

One of the working electrodes was made by plating Pt on titanium foil to study the effect of surface area. Titanium was chosen as a substrate for the deposition of Pt due to its stability to the acidic media and low cost. The electrode was prepared using titanium foil of suitable area (3.96 cm^2) and thickness 0.005 in., soldered to copper wire. The foil was sandblasted uniformly to increase the surface roughness, which enhances the plating. After sandblasting, the Ti foil was cleaned thoroughly to remove any sand or dust particles with acetone, then with distilled water and finally with "ultra high purity water" (Aldrich Chemicals). The solution for plating was prepared using 1 g of hexachloroplatinate salt (Aldrich Chemicals). The salt was dissolved in a known volume of strong acid (1 M HCl) and ultra high purity water in suitable proportions to obtain a plating solution concentration of 0.02 g ml^{-1}. The solution was heated to 60 °C and mixed using an ultrasonic water bath. The platinum was pulse deposited in steps with the deposition current ranging from 5 mA cm^{-2} to a maximum of 20 mA cm^{-2} under galvanostatic conditions for 60 min (each current was held for 15 min with a step change of 5 mA cm^{-2}). The cell deposition potential ranged from −1.3 V (for 5 mA cm^{-2}) to −1.6 V (for 20 mA cm^{-2}) far inside the hydrogen evolution region. By doing this, it was expected that a more porous deposit would be obtained. Intermittently after each pulsing the electrode was weighed to ensure that there was proper plating. A platinum loading of 4.82 mg cm^{-2} was achieved. The electrode was characterized by using scanning electron microscopy, to

Table 1
Compositions of the different electrodes tested showing major and minor component

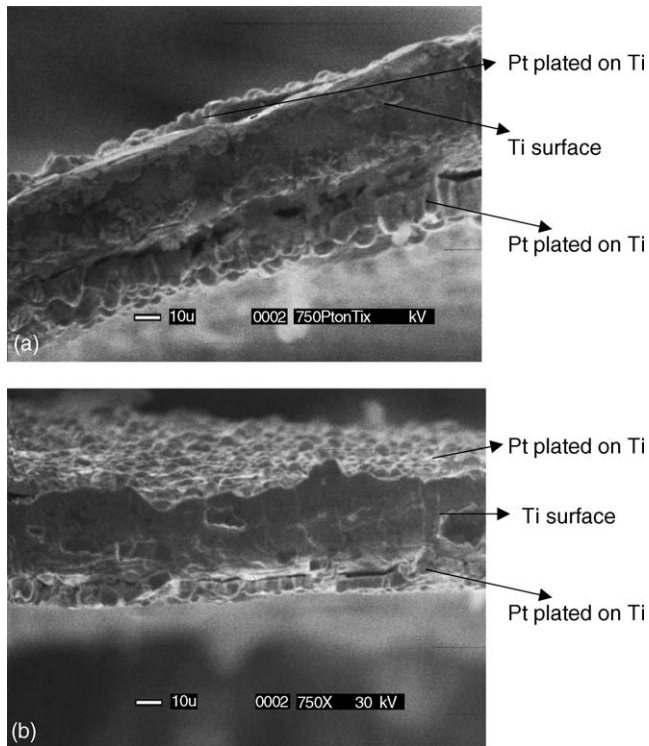| Electrodes	Major metal (wt%)	Minor metal (wt%)
Pt	99.9 (Pt)	–
Pt–Ir	80.0 (Pt)	20.0 (Ir)
Pt–Ru	95.2 (Pt)	4.8 (Ru)
Pt–Rh	80.0 (Pt)	20.0 (Rh)

Fig. 1. Transverse sectional scanning electron photomicrographs for the platinized Pt electrode (magnification 750×, voltage 30 kV). (a) Platinized Pt electrode before testing (approximate thickness 10 μm). (b) Platinized Pt electrode after testing. A rough deposit is observed on the Ti substrate, the deposited platinum seems intact after testing (approximate thickness 10 μm) in the coal electrolytic cell.

ensure the quality of plating as shown in Fig. 1a. A rough deposit of approximately 10 μm (estimated based on the scale of the cross-sectional scanning electron microphotograph) was obtained on the surface of the Ti substrate.

2.2. Polarization experiments

The electrodes prepared from the above method were cleaned with a strong base (NaOH) and with acetone to remove any dust particles on the surface and finally with distilled water. The polarization experiments were carried out in a single compartment glass cell as shown in the Fig. 2 containing 0.12 g ml^{-1} Pittsburgh No. 8 coal suspended in 1 M sulfuric acid with the above mentioned different working electrodes of known surface areas. Before testing, the coal was stored in an argon filled glove box to keep it from exposing to the oxygen which would otherwise form a film on the surface of the coal particles and could possibly lead to an increase in the overpotential for the electrooxidation of the coal. The particle size of the coal used was ranging from 74 to 105 μm. The coal slurry was made by mixing the above coal dust with a specified concentration of 1 M sulfuric acid which acted as electrolyte. Farooque and Coughlin [5] stated that some amount of carbon monoxide was generated along with carbon dioxide at the anode, which might affect our reaction rates when platinum is used as one of the electrodes [12]. Hence, in all the cases, the counter electrode was made of Pt–Ru which is much more resistant to carbon monoxide
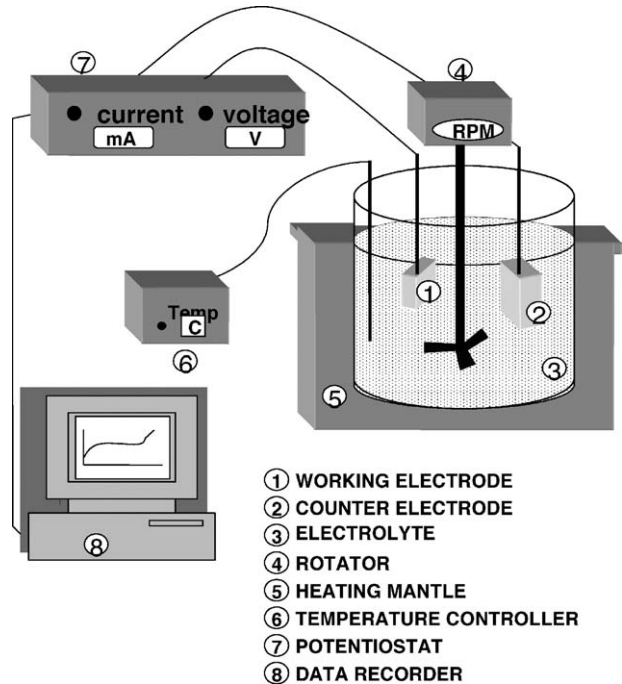

Fig. 2. Schematic representation of the glass cell used for electrooxidation studies of the coal slurries. All the experiments were performed potentiostatically.

poisoning compared to Pt (since electrodes, anode and cathode were immersed in the solution without a membrane). The area of the counter electrode was at least thrice as much as the area of the working electrodes (to keep the anodic reaction limiting). Moreover, in all the experiments temperature, concentration of coal (0.12 g ml^{-1}), particle size (74–105 μm) and impeller speed were kept constant to make a comparative study of only the effect of anodic materials on the electroxidation of coal.

A digitally controlled impeller was used to mix in order to maintain the homogeneity of the coal slurry (the rotation speed was set at 400 rpm). All the experiments were carried out at 40 °C with both electrodes in the same compartment of the cell. Once the cell was set, an ARBIN cycler BT2000 was used to perform the experiments under potentiostatic conditions at different voltages (0.2, 0.4, 0.6, 0.8 and 1 V) and the current developed was recorded. The tests were run for at 100 min with each electrode (each cell potential was held for 20 min). Initially, a baseline experiment with only 1 M H_2SO_4 was carried out to compare the results with coal slurries.

Coal and graphite samples were characterized to determine: particle size, using sieving and surface analysis was investigated by SEM and EDX (JEOL-2300). Gases generated during the gas collection experiments were analyzed using an SRI Gas Chromatograph equipped with a thermal conductivity detector, a HYSEP column and a Mole Sieve column.

3. Results and discussion

3.1. Effect of electrode materials on the electrooxidation of coal

The experiments were performed at 40 °C applying constant cell potentials of 0.2, 0.4, 0.6, 0.8 and 1.0 V with a constant
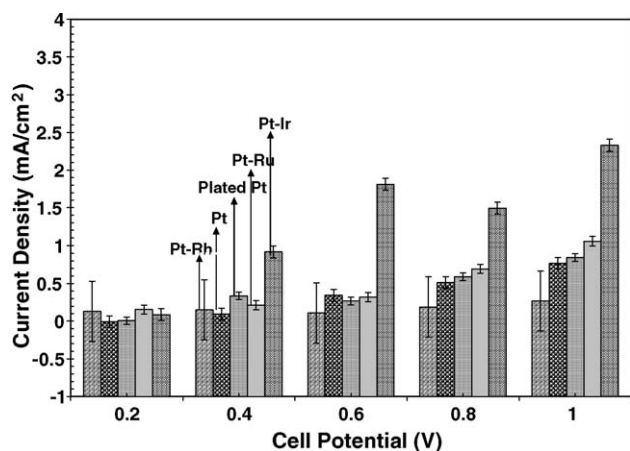
Fig. 3. Average current densities under potentiostatic conditions for different electrodes (anode) Pt, Pt–Ir, Pt–Ru, Pt–Rh and plated Pt at 40 °C for Pittsburgh No. 8 slurry with concentration 0.12 g ml^{-1} in 1 M H_2SO_4. The Pt–Ir electrode over performs the other materials.

mixing of the slurry in a single compartment cell as shown in Fig. 2. Each potential was held constant for 20 min for a total polarization time of 100 min, the results of the average currents developed at each cell voltage are given in Fig. 3. The results shown in Fig. 3 indicate that the current densities generated by all the electrodes were low (0.13–2.33 mA cm^{-2}) which is in agreement with what other authors reported previously [4]. The current densities for coal at different potentials were much higher compared to the background currents for H_2SO_4 (the baseline for H_2SO_4 is not shown in Fig. 3 since its value is too low, 0.00734–0.00283 mA cm^{-2}, compared to the current densities for coal), which indicates that the electrochemical consumption of coal is taking place. The experiments were performed at least three times to evaluate reproducibility. The standard deviations showed that there is a significant error in each of the trials. These differences could be due to several reasons: (1) heterogeneous nature of the coal slurry, (2) turbulence caused due to the rotation of the impeller near the surface of the electrode, (3) the wide range of the coal particle size (74–105 μm) tested, (4) inconsistent evaporation of the solution as time passed and (5) inconsistent collision of the coal particles to the surface of the electrode.

It can be noticed from Fig. 3, that Pt–Ir has the highest current densities while Pt–Rh has the lowest current densities. It has been discussed that Pt–Ir is one of the best electrodes for the electrolysis of water in acidic medium [13], because there is a stable film formation on the surface of the Pt–Ir electrode whose electrical conductivity is very high compared to the film formed on the surface of pure Pt. This could be the possible reason for the better performance of Pt–Ir in the electrolysis of coal slurry. We are currently investigating this aspect in depth in our laboratory (Electrochemical Engineering Research Laboratory at Ohio University, EERL) using molecular modeling and microscopic modeling; the results will be presented in future publications. It can also be seen that with increasing cell potential the current densities increased except for Pt–Ir at 0.8 V there is slight decrease, which could be due to some loss of energy possibly thermal losses, this phenomena is currently being studied at the EERL for further publication.

As explained earlier, one of the electrode was Pt plated on Ti to study the effect of surface area on the electroxidation of coal slurry. From Fig. 3, it can be seen that there is no difference in the current densities between Pt and platinized Pt electrode. This indicates that there is no effect on the electrooxidation even after increasing the surface area (by plating). This means that the electrooxidation of coal depends more on the coal particle surface than the electrode surface area. Based on the results of SEM shown in Fig. 1b (for platinized Pt after polarization) it can be seen that there is no exfoliation or erosion of the plated material. This means that to achieve the same current densities at lower cost it is better to use a platinized Pt electrode which has lower content of noble metal compared to that of pure Pt foil.

3.2. Comparison of coal and graphite electrolysis

In order to have a better understanding of the mechanism for the electrooxidation of coal, i.e. whether only the carbon content of the coal is oxidizing or else even the minor components or impurities present in the coal are aiding the electrooxidation of coal, the performance of coal was compared with the performance of graphite. Several experiments were carried out with pure graphite (SGL carbon) using Pt–Ir (80:20) electrode at different cell potentials (0.2, 0.4, 0.6, 0.8 and 1.0 V) under potentiostatic condition. All the experimental conditions, including the particle size, graphite slurry concentration and temperature were kept same as that for the experiments with coal for better comparison. Only the performance on Pt–Ir electrode at different cell potentials was emphasized since it was observed that Pt–Ir had the better performance compared to other electrodes (see Section 3.1). Each potential was held constant for 20 min for a total polarization time of 100 min, the results of the average currents developed at each cell voltage are given in Fig. 4. From Fig. 4, it can be seen that the current densities in case of coal are higher than the ones observed in graphite. From this it is clear that not only carbon, but also other metallic components, impurities and/or chemical groups in the coal are catalyzing the coal
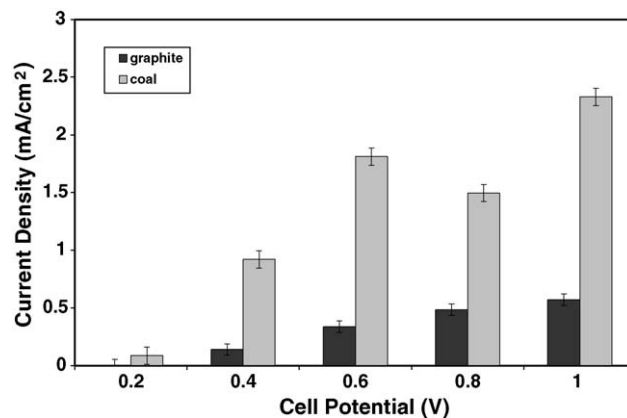

Fig. 4. Average current densities under potentiostatic conditions for Pittsburgh No. 8 and graphite slurries with concentration 0.12 g ml^{-1} in 1 M H_2SO_4 at 40 °C for Pt–Ir (80:20) as anode. The current densities for coal are much higher than for graphite.
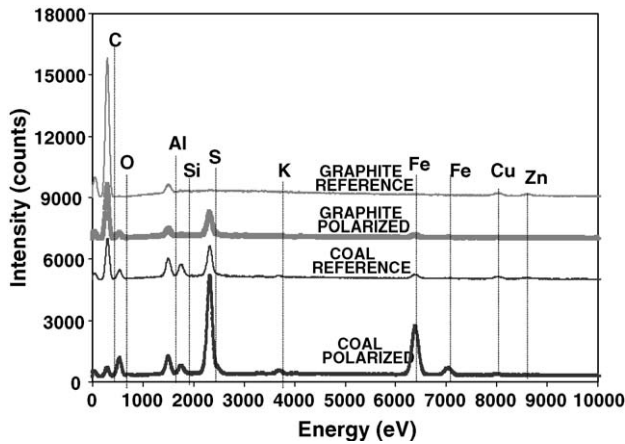
Fig. 5. EDX spectrum for graphite and Pittsburgh Seam No. 8 before and after polarization identifying the main components. Coal contains iron, oxygen and sulfur.

electrooxidation reaction given in Eq. (2). EDX scans were performed to analyze the composition of coal and graphite before and after polarization. The coal and graphite samples were prepared for EDX scans by drying the samples at low temperature of 65–75 °C for 6 h to eliminate the moisture content without affecting the properties of the samples. Fig. 5 shows the EDX spectrum for graphite and Pittsburgh Seam No. 8 coal identifying the main components. It is noticed that the coal contains iron, sulfur and oxygen, while the graphite does not. This indicates that the above main impurities present in the coal may be affecting the reaction. It is possible that the differences in the performance of coal and graphite are due to the presence of iron as reported in the literature [9,10,14,15]; this hypothesis was investigated in Section 3.3. One other observation was that in case of coal and graphite after polarization there was increase in the sulfur peak as compared to that of reference samples (before polarization), this was because of the presence of the sulfuric acid used as electrolyte.

Fig. 6 shows the SEM pictures for coal and graphite. The figure indicates that there is not much difference in the morphology of graphite before and after polarization (see Fig. 6b and d). We could not observe any significant film formation on the surface of the coal, this could be due to shorter test or polarization time (100 min) compared to the other authors [7,9,14]. However, in case of coal (see Fig. 6c) there was agglomeration of the particles which appeared like "cauliflower" after the coal
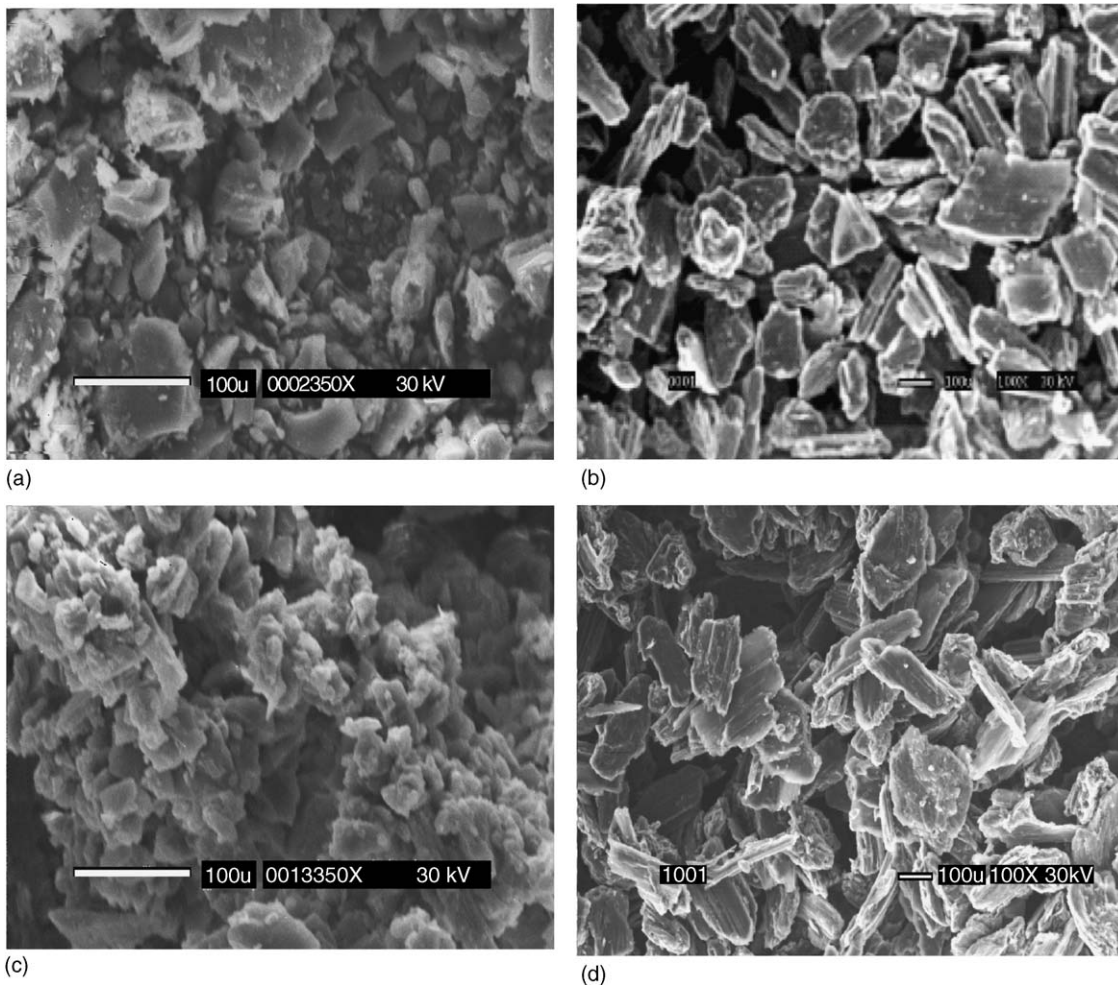

Fig. 6. Scanning electron photomicrographs for coal and graphite before and after polarization. Magnification 350×, voltage 30 kV. (a) Coal particles before polarization, (b) graphite particles before polarization, (c) coal particles after polarization and (d) graphite particles after polarization. Agglomeration of coal particles is observed after polarization.
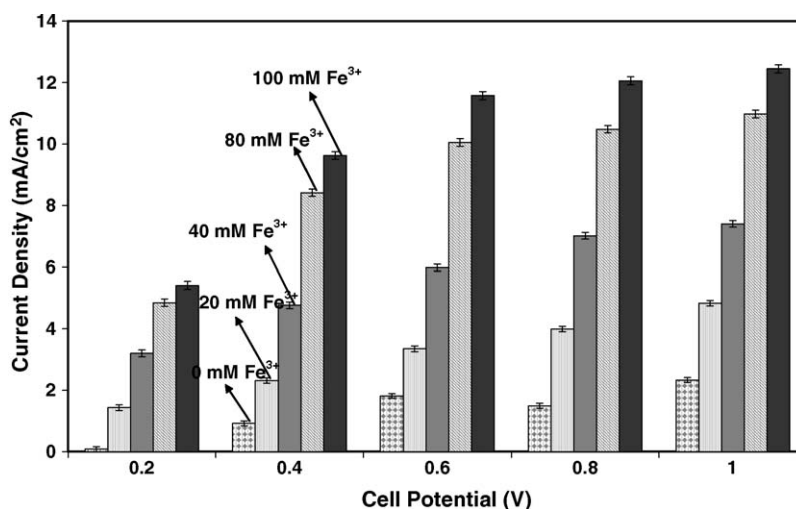
Fig. 7. Effect of Fe(III) added in solution on the electrochemical performance of coal slurries at different operating voltages for Pt–Ir (80:20) as anode. Fe^{3+} has a catalytic effect on the electrooxidation of coal slurries in acidic media.

was polarized which could be possibly due to some tar or oil like chemicals [10] generated during the polarization. In case of graphite, the particles had smooth flat surfaces before testing (Fig. 6b) and there was hardly any difference in the structure after testing (Fig. 6d).

3.3. Effect of iron content in the coal slurry

To further investigate our hypothesis of the effect of iron on the electrooxidation of coal, several experiments were performed by varying concentration of Fe(III). Fig. 7 reflects the effect of adding iron salts(III) in the coal slurries on the electrooxidation of coal, with concentrations of 20, 40, 80 and 100 mM for Pt–Ir (80:20) as anode. The current densities increase with increasing the iron concentration. The electrochemical performance of graphite with a concentration of 100 mM of iron(III) was also evaluated (the results are shown in Fig. 8) for the Pt–Ir electrode, and its performance is compared with the electrochemical respond of coal. As shown in Fig. 8, an increase in the current densities was observed with increasing the concentration of Fe^{3+} for both coal and graphite slurries.
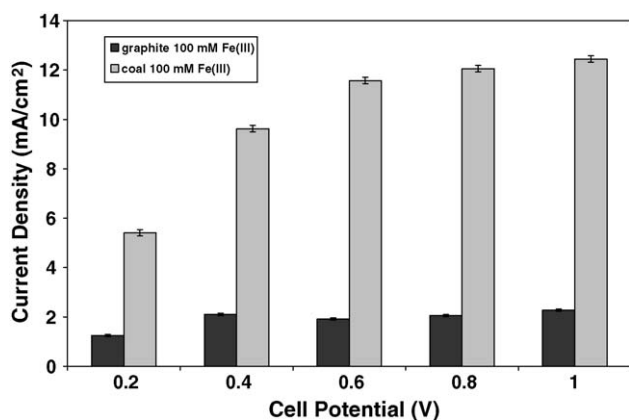

Fig. 8. Effect of Fe(III) added in solution on the electrochemical performance of coal and graphite slurries at different operating voltages. Pt–Ir (80:20) was used as anode. Coal has better performance than graphite.

However, the observed current densities for graphite were not as high as (almost three times less than) that for coal, which indicates that: (1) the iron content in coal is responsible for the higher current densities and (2) the structure and morphology of the coal may also have an influence in the electrochemical performance. We are further investigating this issue and we will present more results in future publications.

According to the results obtained in Fig. 7, we postulated the following mechanism for the electrooxidation of coal in the presence of iron: Fe^{3+} is reduced on the surface of the coal (oxidizing the coal to intermediate chemicals [10] and CO_2) to Fe^{2+}, and Fe^{2+} gets oxidized on the surface of electrode to form Fe^{3+}. We speculate that the contact of coal on the surface of anode is very important, i.e. collision of coal particles on to the anode surface brings the Fe^{2+} next to the electrode. Also, the reduction of Fe^{3+} on the surface of the coal may be enhanced by compounds dissolved from the coal (e.g. the dissolution of the compounds on the surface of the coal could generate active sites on the coal surface for the Fe^{3+} to get reduced) and this dissolution is increased by mechanical abrasion that takes place during coal/electrode collisions as reported by Murphy and Bockris [10]. The proposed mechanism is represented in Fig. 9. If our assumption of the effect of iron content is true, the current densities observed should be enhanced by the presence of Fe^{2+} in solution simultaneously with Fe^{3+}.

The effect of Fe(II) in solution on the electrooxidation of coal on a Pt–Ir (80:20) electrode is shown in Fig. 10. As expected, the presence of additional iron(II) has a positive impact on the current density. There was an increased in the current densities as the potential increased, at 1 V the current density in the presence of 100 mM Fe^{2+} was 27 mA cm^{-2} (see Fig. 10) whereas in presence of 100 mM Fe^{3+} only 12 mA cm^{-2} (see Fig. 8). The increase in the current density due to the presence of Fe^{2+} is in agreement with the results found by Murphy and Bockris [10].

Finally, the synergistic effect of Fe^{2+}/Fe^{3+} was studied. The results for a Pt–Ir (80:20) electrode are shown in Fig. 11, a similar behavior as that of coal slurries with Fe^{3+} or Fe^{2+} was observed but with higher current densities, approximately twice
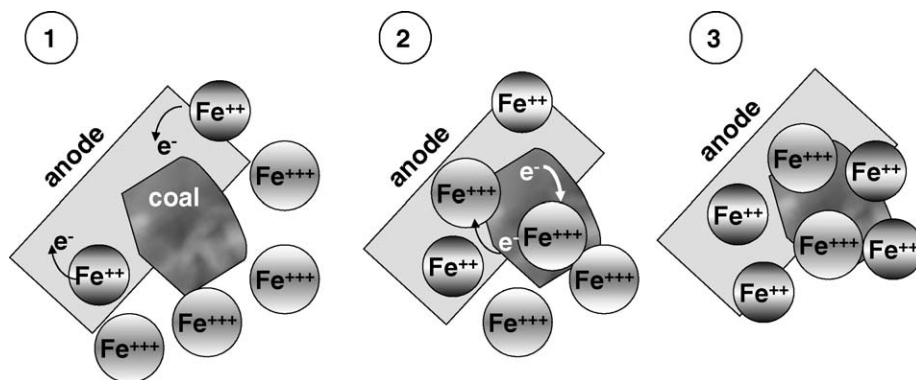
Fig. 9. Schematic representation of the proposed reaction mechanism for the electrooxidation of coal in the presence of Fe^{2+}/Fe^{3+}. (1) Fe^{2+} oxidation at anode, (2) further reduction of Fe^{3+} on the surface of coal regenerating Fe^{2+} and (3) combined iron oxidation–reduction and coal oxidation.

the current densities when either of the species is present. This is a very important finding since the current densities observed were 10–12 times higher than the results reported in the literature [4–6].
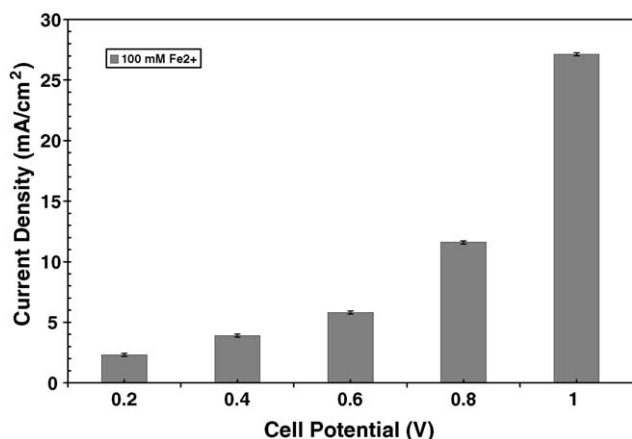

Fig. 10. Effect of Fe(II) on the average current densities of the coal electrolytic cell. The experiments were performed potentiostatically on a Pt–Ir (80:20) electrode at 40 °C, with Pittsburgh No. 8 concentration 0.12 g ml^{-1}, 1 M H_2SO_4 and 100 mM Fe^{2+} concentration. The current densities are higher than in the case of Fe^{3+}.
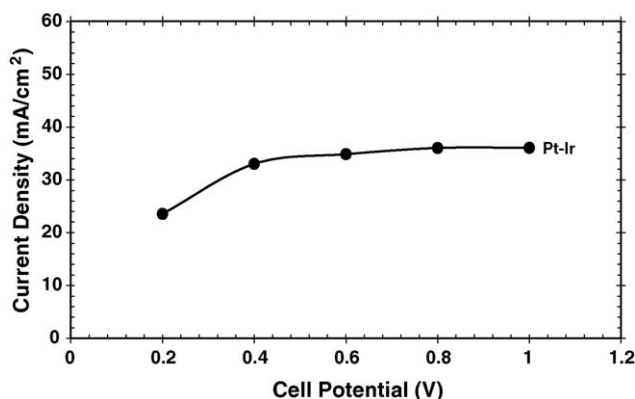

Fig. 11. Effect of Fe(III)/Fe(II) on the average current densities of the coal electrolytic cell. The experiments were performed potentiostatically on a Pt–Ir (80:20) electrode at 40 °C, with Pittsburgh No. 8 concentration 0.12 g ml^{-1}, 1 M H_2SO_4 and 100 mM Fe^{3+}/100 mM Fe^{2+} concentrations. The current density increased due to the synergistic effect of both salts present in the slurry.

3.4. Effect of Ir content on the electrooxidation of coal

Preliminary tests for the optimization of the electrode recipe were conducted. The experiments were performed at the same conditions except that 80 mM Fe(III) was added to the system. The results shown in Fig. 12 indicate that by increasing the iridium content from 20 to 40% the performance of the electrode improved. The current densities were 10–12 mA cm^{-2} for a potential of 0.2–1.0 V. Our group (at EERL) is currently working on determining the optimum iridium content of the electrode; the results will be published in the near future. The cell conditions could also be optimized (by varying Fe concentration, cell temperature, electrode composition, coal concentration, electrolyte concentration and particle size) to operate the cell at no more than 0.6 V at high current densities (at least 100 mA cm^{-2}).

3.5. Efficiency of coal electrooxidation

Gas collection experiments were performed with Pt–Ir (80:20) as the working electrode and Pt–Ru (95.2:4.8) as the counter electrode under potentiostatic conditions at 0.8 V and
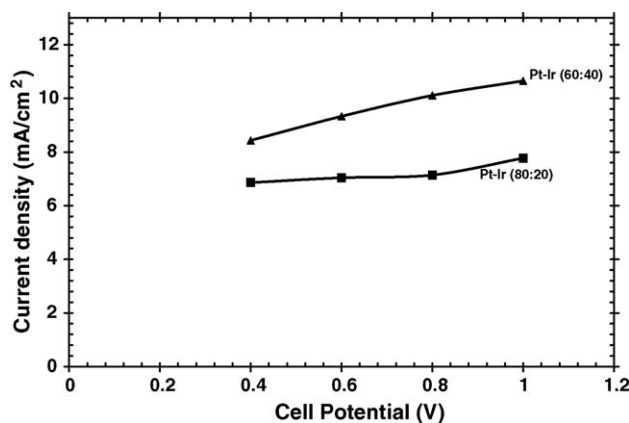

Fig. 12. Effect of electrode composition (Pt–Ir) on the average current densities of the coal electrolytic cell. The experiments were performed potentiostatically on different Pt–Ir electrodes: Pt–Ir (60:40) and Pt–Ir (80:20) at 40 °C, with Pittsburgh No. 8 concentration 0.12 g ml^{-1}, 1 M H_2SO_4 and 80 mM Fe^{3+} concentration. The ratio of Pt–Ir on the electrode can be optimized to increase the average current density of the cell.
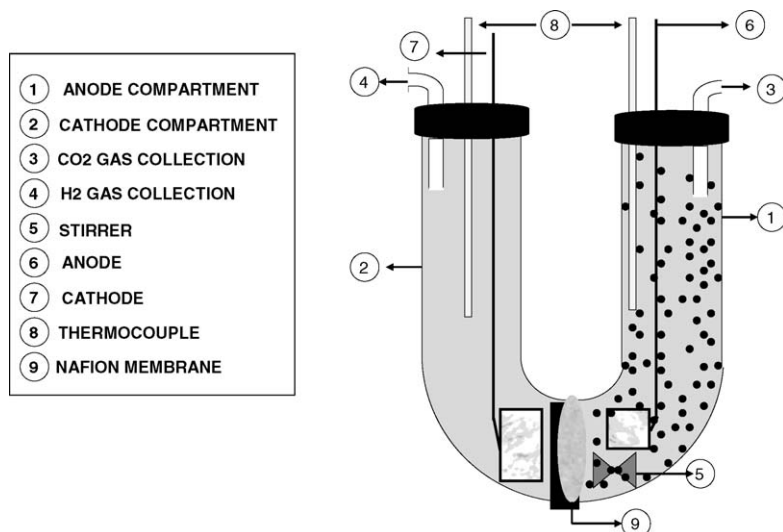
Fig. 13. U-shaped cell designed for the gas collection experiments. The apparatus has two compartments separated by a Nafion membrane. The anode compartment was filled with coal slurry (the slurry was mixed with a stir bar) and the cathode compartment was filled with 1 M H_2SO_4.

40 °C. Coal slurry concentration was $0.12\,g\,ml^{-1}$ with a total volume of 450 ml of the slurry. The solution was mixed using a magnetic stirrer. The tests were performed in a specially designed U-shaped cell as shown in Fig. 13 with two compartments separated by a proton exchange membrane (117 Nafion). Four different experiments were carried out in this set up (the results are shown in Table 2). In each case before the coal was polarized some CO_2 was generated due to chemical oxidation of the coal on the anode side. Once there was almost negligible CO_2 generation due to chemical oxidation, the coal was then polarized as mentioned previously under potentiostatic conditions at 0.8 V. In each case, the polarization test lasted for approximately 24–30 h. The current developed in the coal electrolytic cell decreased with the polarization time. The polarization tests were stopped when the current reached a negligible value (close to 0.0 mA). The efficiency of CO_2 generation was examined and the efficiency of hydrogen generation in all the experiments was assumed to be 100% (since the hydrogen escapes rapidly due to its light weight it was difficult to quantify, however, previous researchers reported 100% faradaic efficiency for the hydrogen evolution [4,5,9]).

3.5.1. Experiment 1: coal slurry

An average current of 4.0 ± 0.2 mA was observed with a test time of approximately 25 h ($90{,}183 \pm 10$ s, this was the elapsed

time to reach 0.0 mA in the cell) for bare coal test slurry. During this period, the amount of gases generated was quantified by downward displacement of water in a gas collection jar. The gas compositions were analyzed using a SRI Gas Chromatograph. Carbon dioxide was observed in both compartments of the cell, this is because of the crossover of CO_2 from the anode to the cathode through the Nafion membrane. The anodic or CO_2 generation efficiency was $18 \pm 3\%$, and the energy consumed for the hydrogen production (assuming 100% efficiency) was $21.44 \pm 0.09\,W\,h\,g^{-1}$ of hydrogen. The chemical oxidation of coal during the first 30 min (before polarization started) produced 12.0 ± 0.5 ml of CO_2. The efficiency in the production of CO_2 is not higher due to the formation of films on the surface of the coal and liquid hydrocarbons as reported by Murphy and Bockris [10].

3.5.2. Experiment 2: coal slurry with Fe^{2+}

A second experiment was performed in which 100 mM Fe^{2+} was added to the coal slurry. The test time was approximately 24 h ($85{,}697 \pm 10$ s, this was the elapsed time to reach 0.0 mA in the cell) with an average current of 25.0 ± 0.2 mA. The chemical oxidation of coal during the first 30 min produced 32.0 ± 0.5 ml of CO_2, which was larger than for the bare coal (12.0 ml). Hence, the anodic or CO_2 generation efficiency is $6.3 \pm 0.4\%$, and the energy consumed for the hydrogen pro-

Table 2
Faradaic efficiency for the electrooxidation of coal on a Pt–Ir (80:20) electrode

Experiment	Average current (±0.2 mA)	Average polarization time (±10 s)	Power consumed (±0.4 s)	CO_2 faradic efficiency on Pt–Ir (80:20) electrode (%)
(1) Only coal	4.0	90183	3.0	18 ± 3
(2) Coal with 100 mM Fe^{2+}	25.0	85697	20.0	6.3 ± 0.4
(3) Coal with 100 mM Fe^{3+}	5.0	103714	4.0	12.9 ± 1.8
(4) Coal with 100 mM Fe^{2+} and 100 mM Fe^{3+}	21.0	108000	17.0	23.5 ± 0.5

The experiments were performed at 0.8 V cell potential, $0.12\,g\,ml^{-1}$ coal slurry concentration, 1 M H_2SO_4 and 40 °C. Pt–Ru (95.2:4.8) was used as the counter electrode.

duction (assuming 100% efficiency) was $21.44 \pm 0.09 \, \text{W h g}^{-1}$ of hydrogen. The faradaic efficiency for the oxidation of coal to CO_2 is lower than in bare coal slurry (see Experiment 1) because the oxidation of Fe^{2+} to Fe^{3+} is also taking place at the electrode, this is the reason why the current developed in this experiment is higher than for the case of bare coal. This finding is important for the production of hydrogen. The higher current will be beneficial for a hydrogen production process because smaller electrodes can be used for the cell. However, if coal is not oxidized (see Eq. (2)) at the same rate that Fe^{2+} is oxidized, the process will not efficiently obtain the hydrogen from the coal (notice that this experiment has the shortest polarization time, see Table 2). This issue can be resolved by combining Fe^{2+} and Fe^{3+} in the slurry as discussed in Experiment 4.

3.5.3. Experiment 3: coal slurry with Fe^{3+}

The third experiment was performed with 100 mM Fe^{3+} in the coal slurry; in this case 22.0 ± 0.5 ml of CO_2 was generated during the chemical oxidation the first 30 min. The test time was approximately 28 h ($103,714 \pm 10$ s, this was the elapsed time to reach 0.0 mA in the cell) with an average current of 5.0 ± 0.2 mA. Hence, the anodic efficiency was $12.9 \pm 1.8\%$, and the energy consumed for the hydrogen production (assuming 100% efficiency) was $21.44 \pm 0.09 \, \text{W h g}^{-1}$ of hydrogen. The current developed in this experiment is smaller than in the case of Experiment 2, because there are not enough Fe^{2+} species in solution to generate a higher current. However, the efficiency for the production of CO_2 is higher than in Experiment 2, which is in agreement with the mechanism proposed in Section 3.3. Furthermore, the total polarization time is longer than in the case of bare coal and coal with Fe^{2+}, which indicates that the presence of Fe^{3+} increases the efficiency in the production of hydrogen from coal.

3.5.4. Experiment 4: coal slurry with Fe^{2+}/Fe^{3+}

Finally, the synergistic effect of Fe^{2+}/Fe^{3+} was tested by adding 100 mM of each species. The test was performed for 30 h ($108,000 \pm 10$ s, this was the elapsed time to reach 0.0 mA in the cell) with an average current of 21.0 ± 0.2 mA and it was observed that the efficiency for the complete oxidation of coal to CO_2 was the highest. A volume of 50.0 ± 0.5 ml of gas was collected at the anode due to chemical oxidation during the first 30 min, so not only the electrolytic generation of gases increased but also the gas generation due to chemical oxidation as well. The increase in the oxidation rate of coal due to the synergistic effect of Fe^{2+}/Fe^{3+} is in agreement with the mechanism proposed in Section 3.3. Similarly, the anodic efficiency is $23.5 \pm 0.5\%$, and the energy consumed for the hydrogen production (assuming 100% efficiency) was $21.44 \pm 0.09 \, \text{W h g}^{-1}$ of hydrogen. This finding indicates that the concentration of coal, Fe^{2+} and Fe^{3+} can be optimized to improve the conversion of coal to CO_2 and increase the efficiency in the production of hydrogen from coal electrolysis. Results on this topic will be presented in future publications.

4. Conclusions

The electrolysis of coal slurries was tested with five different electrodes, of which Pt–Ir had the best performance. Furthermore, the electrolysis was also compared with pure graphite to determine if any components or impurities present in the coal affected the electrooxidation of coal. It was found that both iron(III) and iron(II) affect the electrooxidation of coal. The synergistic effect of Fe^{2+}/Fe^{3+} showed high current densities for Pt–Ir approximately 10–12 times higher current densities than the ones reported in the literature [4–6]. Even the gas collection experiments for coal containing both iron(II) and iron(III) showed the highest efficiencies for CO_2 and H_2 generation with an approximate energy consumption of $22 \, \text{W h g}^{-1}$ of hydrogen. It is expected that by optimizing the electrode recipe, the performance of the coal electrolytic cell can be further enhanced since the Pt–Ir (60:40) has higher current densities as compared to that of Pt–Ir (80:20). Also, whether the high currents observed in the presence of additional iron(III) and iron(II) are true representation of the electrooxidation of coal or else there is any side reaction undergoing, is still very uncertain. Even the other species present in coal might be affecting the electrooxidation of coal hence the true mechanism and the rate limiting step are yet a matter of discussion. Further analysis and investigation of the mechanism is undergoing at our research lab (EERL).

4.1. Applications of coal electrolysis and comparison with water electrolysis

It is foreseen that the electrolysis of coal slurries can be used for distributed hydrogen production sites (1000 kg of H_2 per day [3]) or for the production of hydrogen on-site (e.g. small hydrogen generators to be used in residential houses). The advantage of this process is its ease of integration with renewable energy (electricity) sources. Because the energy consumption is low, the cell could operate with renewable energy. Therefore, hydrogen could be produced on demand, minimizing the needs for hydrogen storage. The theoretical energy consumption during coal electrolysis (assuming that there are not kinetics limitations for the reaction to take place at the thermodynamics conditions) can be calculated from the standard potential of the cell and is equal to $5.6 \, \text{W h g}^{-1} \, H_2$, while the electrolysis of water requires at least $33 \, \text{W h g}^{-1} \, H_2$ at standard conditions, this means that theoretically the electrolysis of coal consumes 83% lower energy than a water electrolyzer. The scalability of the technology as well as its ability to easily operate in an on-demand mode facilitates the technology's ability to interface with renewable energy sources including those whose production of electricity may vary with time (for example, wind and solar energy).

The results of this study indicate that hydrogen can be produced from the electrolysis of coal at 0.8 V with an energy consumption of $22 \, \text{W h g}^{-1} \, H_2$, this energy is 52% lower than the energy consumed in a commercial water electrolyzer ($46 \, \text{W h g}^{-1} \, H_2$, assuming a cell voltage of 1.7 V). Lower energies could be obtained by the optimization of the variables mentioned earlier (electrode composition, iron concentration, temperature, coal particle size and coal concentration).

4.2. Preliminary economics analysis

Assuming that solar energy is used at a cost of US$ 0.21 kW h^{-1} [16] and setting the price of coal at US$ 42 tonne^{-1} hydrogen can be produced from the electrolysis of coal at US$ 1.2 kg^{-1} of H$_2$, if the cell operates at 0.8 V (22 W h g^{-1} of H$_2$). On the other hand, hydrogen obtained by the electrolysis of water using solar energy will cost US$ 9.8 kg^{-1} of H$_2$, if the cell operates at 1.7 V (46 W h g^{-1} H$_2$). The back of the envelope calculations indicate that the production of hydrogen from coal electrolysis can be up to 88% cheaper than from the electrolysis of water, assuming that both cells have the same production costs. Detail calculations and economics analysis including capital investment, fixed and variable costs, and return of investment will be presented in future publications. However, the preliminary economics values indicate that the electrolysis of coal can be a potential solution for the production of hydrogen on-site, once the technological challenges (discussed in this paper) are addressed.

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