Understanding the kinetics of coal electrolysis at intermediate temperatures

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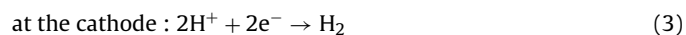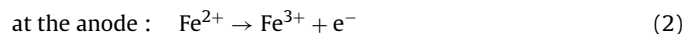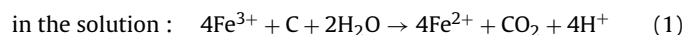
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ABSTRACT

The kinetics of coal electrolysis was studied on a bench continuous coal electrolytic cell setup at intermediate temperatures by applying galvanostatic polarization techniques. The results showed that coal oxidation takes place during the contact of the coal particles with the electrode and it is directly related to electrode composition and the presence of Fe(III) ions in the slurry solution. Coal electro-oxidation by Fe(III) is the limiting step in the oxidation of a $0.02\,g\,mL^{-1}$ coal slurry containing $100\,mM$ Fe(II)/Fe(III) at high currents ($100\,mA$) at $108\,°C$ with a $65\,mL\,min^{-1}$ flow rate. The study suggests that the films that grow at the surface of the coal particles limit the coal conversion. A mechanism is proposed to describe the coal oxidation process.

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1. Introduction

Hydrogen production via coal electrolysis was evaluated at intermediate temperature (80–108 °C) on a bench-scale continuous setup in a previous paper [1]. It was found that increasing temperature significantly increases the coal conversion and coal oxidation rate. However, the coal conversion still requires improvement (3.2% at 108 °C) to achieve values as high as from coal gasification. Understanding the kinetics of coal electrolysis is required in order to further improve the coal conversion. The mechanism of coal electrolysis is complicated and difficult to determine due to the complex structure and components of coal. Previous kinetic studies are limited, and no progress in understanding the mechanism of coal electrolysis has been made in the past 30 years. A number of researchers proposed that the anodic current of coal electrolysis was mainly attributed to Fe(II) ions leached into the solution from the carbonaceous components of the coal [2–8]: Fe(II) is oxidized to Fe(III) at the anode; Fe(III) mediates coal oxidation and is reduced back to Fe(II). On the other hand, the cathodic current is attributed to the reduction of protons. This process can be represented by the reactions shown in Eqs. (1)–(3):

$$\text{in the solution}: \quad 4Fe^{3+} + C + 2H_2O \rightarrow 4Fe^{2+} + CO_2 + 4H^+ \quad (1)$$

$$\text{at the anode}: \quad Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (2)$$

$$\text{at the cathode}: 2H^+ + 2e^- \rightarrow H_2 \quad (3)$$

The standard potential of electro-oxidation of Fe(II) to Fe(III) is 0.77 V vs. SHE, which is close to the experimental cell voltage of coal electrolysis (0.75–1.0 V) [9]. This fact further confirms that iron ions play an important role in coal electrolysis. According to Eqs. (1) and (2), the reactions that take place in the anodic compartment of the cell include Fe(II) electro-oxidation and chemical oxidation of coal. Former researchers [4–8] indicated that the coal oxidation rate is much slower than the Fe(II) oxidation rate. Therefore, a kinetics study should concentrate on the coal oxidation.

Anthony and Linge [2] indicated that the oxidation of coal by Fe(III) (Eq. (1)) is a chemical oxidation and involves several reaction steps: (1) Nernst-layer or pore diffusion of Fe(III) to reaction sites of the coal particle; (2) Fe(III) adsorption and reduction at each site; (3) de-adsorption and diffusion of the Fe(II) and other dissolved reaction products.

In 1992, Tomat et al. [10,11] reported that the limiting current of coal electrolysis increased with coal concentration and they explained that the increase of the anodic current may be ascribed either to a charge transfer on coal particles colliding with the electrode, or to oxidation of some organic or inorganic components of the coal (soluble in hot electrolyte, e.g., H_3PO_4). To verify these two hypotheses, the coal was filtered off from the solution, and the electrochemical activity of the filtrate was shown to be unchanged with that of the coal slurry solution. This result indicated that the anodic current of coal electrolysis could be ascribed to the oxidation of the reactive compounds leached from the original coal, not to the collision between coal particles and electrode. Other researchers achieved similar results [3–6,8]. However, their conclusions were based on experiments carried out at low temperatures and for short time (based on cyclic voltammetry response). Possible explanations for the increase in the anodic current with coal concentration as

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reported by Tomat et al. [10,11] are: (1) within several minutes and at low operating temperatures, kinetics of coal oxidation is slow and can not be observed; (2) dissolved Fe(II) concentration increased with coal concentration, which may be responsible for the increased the anodic current. Therefore, these results are not enough to verify that the dissolved components from the coal are responsible for its oxidation.

Dhooge and Park [4–6] compared the electrolysis results of graphite and coal, and pointed out that coal particles contain the reactive sites that can be oxidized by Fe(III), which are not present in graphite. Thomas et al. [12] reported that each coal particle has three different types of reactive sites: (1) at the external surface of the coal, (2) at the internal pore surface, and (3) within the solid coal matrix. The authors proposed that, at short reaction time, coal oxidation only took place at the exposed coal surface (type 1); at long time, Fe(III) becomes accessible to type 2 reactive sites. It would take much longer time for Fe(III) ions to reach the type 3 reactive sites or the Fe(III) could reach those reactive sites when coal particles are cracked and type 3 reactive sites become type 1 or 2. The authors believed that the coal oxidation took place at the surface of the coal particles or internal pores of the coal particles. It should be pointed out that if coal oxidation takes place in the internal pores of the coal particles, then its oxidation is only chemical, and it should be independent of the electrode used in the electrochemical cell.

Okada et al. [8] studied coal electrolysis in 4.15 M H_2SO_4, and concluded that with the presence of Fe(II), the anodic current is predominately Fe(II) oxidation. Without the presence of Fe(II), coal was oxidized by the following two approaches: (1) direct collision of coal particles with the electrode to produce CO_2; and (2) the oxidation of the dissolved products of coal. The results reported by Okada et al. [8] indicate that coal can be electrochemically oxidized without iron ions.

Sathe and Botte [13] compared the electrolysis of coal on two different type of electrodes: carbon fiber electrode and carbon fiber electrode plated with Pt–Ir. The authors reported that the coal oxidation was only observed on the plated carbon fiber electrode. This phenomenon justified the electro-oxidation of the coal, because chemical oxidation will be independent of the electrode type. They also observed that the electro-oxidation of coal is enhanced by the presence of graphite particles in the slurry. The authors hypothesized that the graphite particles tend to remove the films that grow on the surface of the coal particles that inhibit its electro-oxidation with time.

Patil et al. [14] evaluated the effect of Fe(II) and Fe(III) on coal electrolysis at 40 °C, and proposed a mechanism for coal oxidation. The authors postulated that the contact of coal particles with the electrode increases the coal oxidation rate. They attribute the results to: (1) the concentration of Fe(III) is higher at the electrode surface than in the bulk; (2) the reduction of Fe(III) could be enhanced by compounds that are dissolved or leached from the coal surface; (3) the process may be speeded by the mechanical abrasion that takes place during coal/electrode collisions.

According to Patil et al. [14], coal oxidation is a combination of coal particle oxidation and dissolved components oxidation. However, as indicated in the previous paper [1], the coal oxidation rate is very slow and cannot be significantly observed at 40 °C. In addition, the flow pattern in their setup was not favorable for the contact between the coal particles and the electrode. Therefore, the results reported are limited to the operating conditions and the setup. In addition, they did not point out if the reactions observed were chemical or electrochemical.

The literature review shows that there is no common knowledge on the oxidation and/or electro-oxidation of coal. Some authors report coal oxidation, others indicate electro-oxidation, and some indicate a combination of both. In order to clarify the mechanism for the electrolysis of coal, it is necessary to perform a through

analysis of the kinetics. Based on the results reported in the previous paper [1], coal oxidation (0.02 g mL^{-1} coal, 4 M H_2SO_4 as the electrolyte with 100 mM Fe(II)/Fe(III)) was only observed at temperatures higher than 80 °C when applying 100 mA current in the cell (anode and cathode were 2 cm diameter). Therefore, the goal of this paper is to investigate the kinetics of coal oxidation at intermediate temperatures (above 100 °C). Answers to the following questions are attempted: (1) does CO_2 evolved during the reaction come from coal particles or from dissolved active components of coal? (2) Is coal oxidized by Fe(III) through chemical oxidation or electro-oxidation? (3) Can coal particles be oxidized without iron ions, as indicated in the literature [8]?

2. Experimental

The experiments were carried out in a bench-scale continuous coal electrolytic cell (CEC) described in our previous paper [1]. The CEC was composed with the same anode and cathode electrodes used in previous publication [1] (2 cm diameter electrodes, anode contained 5.3 mg of Pt–Ir per centimeter of carbon fiber bundle, while the cathode contained 6.0 mg of Pt per centimeter of carbon fiber bundle, 36.8 and 39.2 cm of carbon fiber bundle were used for the anode and cathode, respectively). BASF polyacrylonitrile (PAN) carbon fiber (from Celion G30-500, 7 μm diameter) were used as substrates for the anode and cathode of the CEC, respectively. A complete description of the experimental procedure and materials used to make the electrodes is given in the literature [1]. Pittsburgh No. 8 coal (sample DECS-12 from Penn State Coal Bank) was used to prepare the coal slurry. The coal slurry concentration was 0.02 g mL^{-1} and the particle size was kept between 74 and 105 μm. Concentrated sulfuric acid (4 M) was used as the electrolyte to increase the bubble point of the solution, this allowed to operated between 100 and 108 °C with minimum vaporization of the electrolyte. Reagent grade crystal $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot H_2O$ (from Fisher Scientific) were used as the source of iron ions. Concentrations of Fe(II) and Fe(III) were adjusted in the slurry in order to evaluate their effect on the kinetics of coal oxidation. The concentrations of Fe(II) and Fe(III) in solution were measured using a rotating disk polarization method [15,16]. The volume of anodic and cathodic solutions was kept at 300 mL. The flow rate of the coal slurry solution was maintained at 65 mL min^{-1} to guarantee sufficient contact between the solutions and the electrodes. Gas samples were collected at the cathode and anode reservoir by water displacement. Gas composition was analyzed by using a gas chromatograph instrument (from SRI Instruments, CA), equipped with a thermal conductivity detector, 2 m long HYSEP column and 1 m long molecular sieve column. The temperature of the instrument was set to change from 50 to 200 °C, in order to detect gases such as H_2, O_2, N_2, CO, and CO_2.

Different currents (from 100 to 5 mA) were applied for coal electrolysis during the study in order to electroxidize the coal slurry with or without iron additives. Galvanostatic experiments were performed on the CEC and the cell voltage was measured using a Solartron potentiostat (S1 1287 electrochemical interface). Experiments were terminated when the cell voltage reached 1.1 V to avoid water electrolysis and possible oxidation of the electrode support (Hastelloy, which contains 57.5% nickel).

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

3. Results and discussion

3.1. Evaluation of the reservoir temperature and cell temperature

As indicated in previous paper [1], temperature enhanced the kinetics of coal electrolysis. Determining the effect of temperature
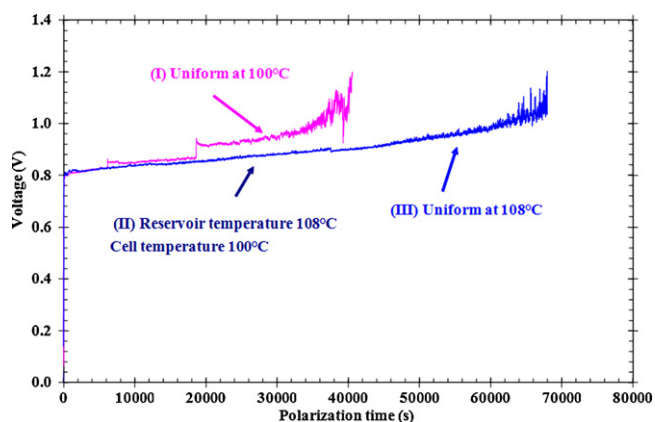
Fig. 1. Effect of the cell temperature and temperature of the reservoirs on coal electrolysis at 100 mA applied current. Anolyte solution consisted of 0.02 g mL^{-1} coal with 4 M H$_2$SO$_4$ as the electrolyte and 100 mM Fe(II) and 100 mM Fe(III). Curve (I): polarization experiment at uniform temperature of 100 °C; curve (II): polarization experiment at cell temperature of 100 °C and reservoir temperature of 108 °C; curve (III): polarization experiment at uniform temperature of 108 °C.
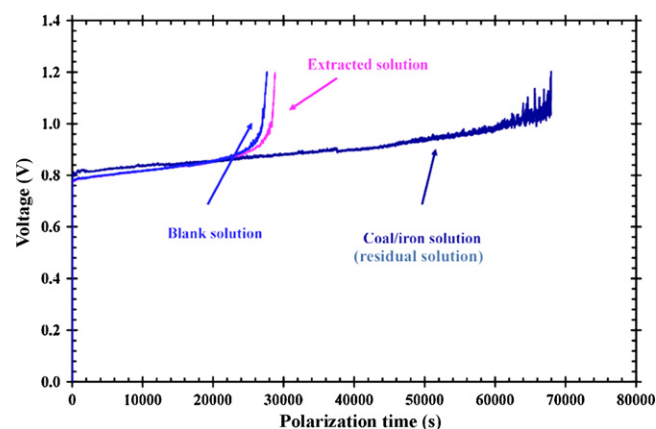
Table 1
Gas concentration changes during the extracting and heating process of the coal slurry solution.

Time (h)	Gas volume (± 1 mL)	H$_2$ (%)	O$_2$ (%)	N$_2$ (%)	CO (%)	CO$_2$ (%)
0	100	0	22.50	77.46	0	0.04
2	141	0.18	26.21	73.11	0.04	0.46
4	141	0	26.68	72.84	0.04	0.44
6	142	0.51	26.53	72.68	0.03	0.25
8	142	2.39	27.27	69.94	0	0.40

in the performance of the CEC and the temperature change in the process reservoirs can help in the elucidation of the mechanisms involved in the oxidation of coal. For instance, if the temperature in the CEC affects the oxidation of coal, then the process is mostly driven by an electrochemical reaction and a temperature change in the process reservoirs would not cause a significant change in the performance. Three experiments were carried out for a coal slurry containing: 0.02 g mL^{-1} coal, 100 mM Fe(II) and 100 mM Fe(III), and 4 M H$_2$SO$_4$ electrolyte. The CEC was operated galvanostatically at 100 mA. The experimental set up used allows controlling the temperature of each reservoir and the cell temperature, separately. Experiment (I) was performed at a uniform temperature of 100 °C (reservoirs and cell), experiment (II) was performed at 108 and 100 °C for the reservoirs and cell temperature, respectively, and experiment (III) was performed at a uniform temperature of 108 °C (reservoirs and cell). The polarization results are shown in Fig. 1. The polarization time (40,563 s) for experiment (I) was almost same as that for experiment (II) (40,975 s), while the polarization time (67,972 s) for experiment (III) was much longer. The results indicate that the cell temperature significantly affected the polarization time of the coal slurry solution, while the temperature of the reservoir did not affect the coal oxidation within the range of temperatures used during the experiments.

The results suggest that the limiting reaction of coal oxidation occurs in the cell, not in the bulk solution. The findings are in agreement with the results reported by Sathe and Botte [13] and Jin and Botte [1], in which the composition of the electrode had a significant effect on the oxidation of coal, indicating that an electro-oxidation reaction is involved in the process.

3.2. Evaluation of the extracted solution and residual solution

According to the literature reactive components that leach out from coal and dissolve in the electrolyte are responsible for part or all of coal oxidation [10,11]. In order to evaluate the oxidation of dissolved components, galvanostatic experiments were carried out with a blank solution, an extracted solution with iron ions, and a residual solution with iron ions at 108 °C. The blank solution consisted of 100 mM Fe(II) and 100 mM Fe(III) with 4 M H$_2$SO$_4$ as the electrolyte. The extracted and residual solutions were prepared as follows:

(1) Coal slurries were prepared with 0.02 g mL^{-1} of coal and 4 M H$_2$SO$_4$ electrolyte solution.

(2) The slurries were heated and stirred in a sealed flask at 108 °C for 8 h (experimental apparatus described in Fig. 5 of a previous paper [1] was used), at the same time, the gases evolved during the experiment were collected, results are reported in Table 1.
(3) The solution was cooled down to ambient temperature and the coal particles were removed from the slurry by filtration using a 12.5 cm diameter fine filter paper from Fisher Scientific (Cat. 09-790-4E) and a Coors filtering crucible for bitumen (faucet-water vacuum method).
(4) The solution collected through the filter constitutes the "extracted solution," which contains all the dissolved components from the coal extracted at the operating conditions described in step (2).
(5) The coal particles collected in the filter paper were washed with distilled water, and the washed coal particles were mixed with 4 M H$_2$SO$_4$ to constitute the "residual slurry solution."
(6) Finally, the extracted and residual solutions were both added iron salts to obtain 100 mM Fe(II) and 100 mM Fe(III) concentration.

The galvanostatic results of the three solutions (blank, extracted, and residual) at 100 mA are shown in Fig. 2. As indicated in the figure, the polarization times are 29,030, 29,794, and 67,825 s, for the blank, extracted, and residual solutions, respectively. The concentration of Fe(II) and Fe(III) were measured before and after the electrolysis and the results are reported in Table 2 (see Experiments # I, II, and III). The results show that the polarization time for the extracted solution is slightly longer than for the blank solution. According to Faraday's law, it can be attributed to the iron ions leached from the coal. However, the polarization time for the residual solution is much longer than for the blank solution, in addition, the polarization time is the same as that of fresh coal slurry (0.02 g mL^{-1}) with 4 M sulfuric acid and 100 mM Fe(II) and 100 mM Fe(III) as reported in the previous paper, see Fig. 8 of Xin and Botte [1]. The results demonstrate that the differences between the blank solution and the residual solution are mainly attributable to the oxi-

Fig. 2. Galvanostatic polarization of blank, extracted, and residual solutions at 108 °C, and 100 mA.

Table 2

Concentration of iron ions before and after coal electrolysis. The experimental errors for the iron ion concentrations are 1 mM for concentrations lower than 10 and 5 mM for concentrations above 100 mM.

Experiment #	Solution type	Added Fe(II)/Fe(III) (mM)	Fe(II)/Fe(III) measured[a] before (mM)	Fe(II)/Fe(III) measured[a] after (mM)	Applied current (mA)	Predicted polarization[b] time (s)	Experimental polarization time (s)
I	Residual solution	100/100	99/100	2/199	100	28,077	67,825
II	Blank solution	100/100	99/101	0/200	100	28,657	29,030
III	Extracted solution	100/100	101/101	0/201	100	29,236	29,794
IV	Original solution	0/0	2.42/2.54	0.81/5.06	35	1331	628
V	Extracted solution	0/0	2.42/2.54	0/5.91	35	2001	2418
VI	Residual solution	0/0	0/0	0/0	0	0	150
VII	Residual solution	8/8	8.05/7.95	2.1/14.98	35	4920	65,914
VIII	Residual solution	0/16	0/16.04	2.2/15.01	0	0	31,564

[a] Iron concentrations measured using the rotating disk method described in previous paper [15].
[b] Predicted polarization time based on Faraday's law and the concentration of Fe(II) present in solution.

dation of coal particles and that there are no reactive components leached out from the coal that can be electro-oxidized under the operating conditions used, except for iron ions. The coal particles seem to be the major reactive component of the coal oxidation.

The gas composition analysis during the heating process (Table 1) shows that trace CO, H_2 and CO_2 are produced during the chemical oxidation of coal. O_2 and N_2 detected are from air. As coal is oxidized the concentration of CO decreases and the concentration of CO_2 increases. The analysis suggests that CO is an intermediate product of the chemical oxidation of coal, which continues oxidizing to produce CO_2 in the presence of air. It is important to notice that the volume of the hydrogen collected during the experiments was low ($142 \times 2.39\% = 3.39$ mL according to Table 1).

The results indicate that chemical oxidation is not the major contribution to the coal conversion during the electrolysis of coal at the operating conditions used. Therefore, it can be concluded that coal oxidation takes place on the surface of the electrode, and that coal particles are the major component during the reaction. Subsequently, the coal electro-oxidation takes place at the surface of the coal particles and not at the internal pores of the particle, because there is no contact between the internal surfaces with the electrode surface.

It is worth pointing out that 100 mM Fe(II) and 100 mM Fe(III) were always added into the analyte solutions to sustain the applied experimental current (100 mA) under current operating conditions used. In order to further understand the kinetics of coal oxidation, it is necessary to determine the role of iron ions during coal oxidation.

3.3. Effect of iron ions concentration

As previously reported [1,14], iron ions play an important role on the electrolysis of coal, however, it is not clear how the iron ions affect the coal oxidation. In order to study the iron ion effect on coal oxidation, evaluation of the coal electrolysis process with different iron concentrations was carried out. The results could also be used to determine an optimized concentration of iron ions for experimental scale-up and industrial applications. Fig. 3 presents the galvanostatic experimental results of the 0.02 g mL^{-1} coal slurry solutions containing different concentrations (20, 40, and 100 mM) of both iron ions, Fe(II) and Fe(III), at 108 °C (4 M sulfuric acid electrolyte). The results show that the polarization time of coal electrolysis increases with the iron concentration, which indicates that the coal conversion increases with the iron concentration. However, it is not practical to increase the coal conversion by adding iron ions.

Table 3 presents the effect of iron ions concentration on the CO_2 Faradaic efficiency for the polarization results shown in Fig. 3. The Faradaic efficiency calculation method to estimate the coal conversion to CO_2 was reported in the previous paper [1]. It was found that the slurry containing 40 mM iron ions has the highest Faradaic effi-
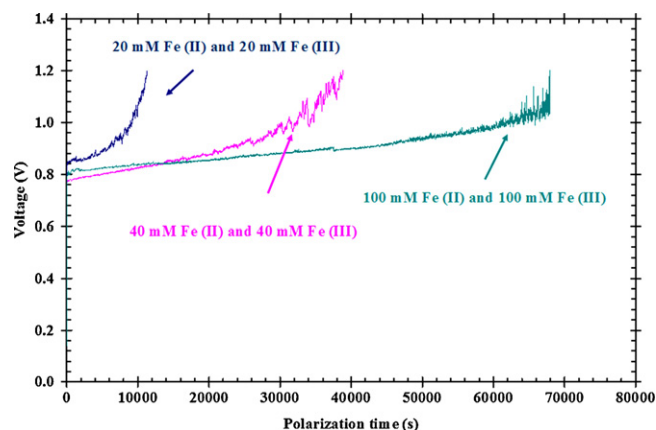
Fig. 3. Galvanostatic performance of coal slurries (0.02 g mL^{-1} coal and 4 M H_2SO_4 as electrolyte) containing different concentrations of iron ions (20, 40 and 100 mM) at 100 mA and 108 °C. The results show that high iron concentration oxidized more coal; however, 40 mM iron ions solution had the highest CO_2 Faradaic efficiency (see Table 3).

ciency when compared to the slurries containing 20 and 100 mM iron ions. The slurry with the lowest iron concentration, 20 mM iron ions, has a 48.7% Faradaic efficiency, this indicates that the oxidation of coal contributes with less than 50% to the anodic current, while the Fe(II) oxidation contributes with more than 50% to the anodic current.

In practice, it is expected that coal should be oxidized without adding any iron ions under 1.2 V. In order to test this possibility, galvanostatic tests were carried out for 0.02 g mL^{-1} coal slurry solution without adding iron ions (100 mA current and 4 M H_2SO_4) at two different temperatures (80 and 108 °C). The results (shown in Fig. 4) indicate that the polarization times for the coal electrolysis are short at both temperatures, 80 °C (1 min) and 108 °C (4 min). The short oxidation times may be a contribution of the oxidation of iron ions leached out from the coal. The results showed that coal could not be oxidized to CO_2 without enough iron ions at 100 mA polarization current under the described operating conditions (temperatures 108 °C, 0.02 g mL^{-1} coal slurry solution, 65 mL min^{-1} flow rate, and 2 cm diameter cell electrodes).

Table 3

Effect of iron ion concentration on CO_2 Faradaic efficiency.

| Fe(II) (mM)/Fe(III) (mM)	20/20	40/40	100/100
Testing time (± 1 s)	11,317	38,825	67,972
Calculated time (± 1 s)	5806	11,612	29,030
η_{CO_2}%	48.7	70.1	57.3
Coal oxidation time (± 1 s)	5511	27,213	38,942
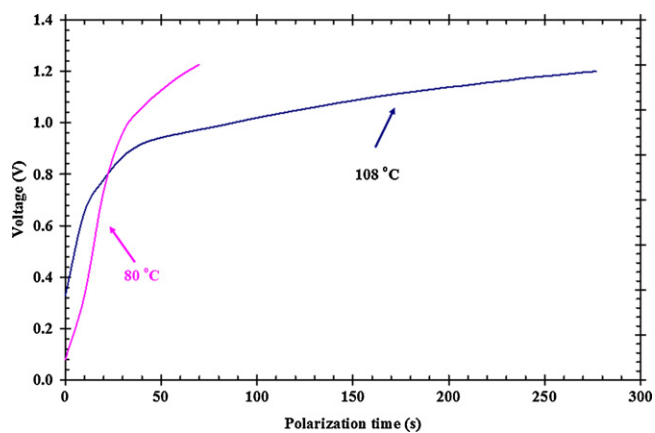
Fig. 4. Galvanostatic performance of coal slurries without added iron ions at 100 mA applied current. Anode solution is a 0.02 g mL^{-1} coal solution with 4 M H$_2$SO$_4$ as the electrolyte. The experiments were performed at 80 and 108 °C separately. The results showed that without adding iron ions, coal could not be oxidized at 100 mA applied current under a cell voltage below 1.2 V.

In conclusion, although the temperature increased the CO$_2$ Faradaic efficiency and coal conversion rate, the effect is insignificant when compared with the effect of iron ions on coal electrolysis. Without adding iron ions, the coal oxidation current will be much lower than 100 mA. So it is not practical to analyze the effect of iron ion on the mechanism of coal oxidation at 100 mA polarization current, because the coal oxidation cannot be observed without adding iron ions at this operating condition. Therefore, evaluation of the coal oxidation at lower currents was carried out accordingly (see Section 3.4).

3.4. Polarization experiments on coal slurries at low currents

As indicated above, the original coal slurry solution without any additives (iron ions) cannot be oxidized at 100 mA applied current under the described operating conditions. So polarization experiments with lower currents were carried out for "original coal slurry" solutions (coal and H$_2$SO$_4$). In order to choose the appropriate polarization current, several polarization experiments were performed to a 0.02 g mL^{-1} coal slurry solution with 4 M H$_2$SO$_4$ as electrolyte under different currents ranging from 15 to 40 mA. The results are shown in Fig. 5. The results indicate that the original coal slurry solution cannot support currents higher than 40 mA. Therefore, 35 mA was chosen as the initial start current for the
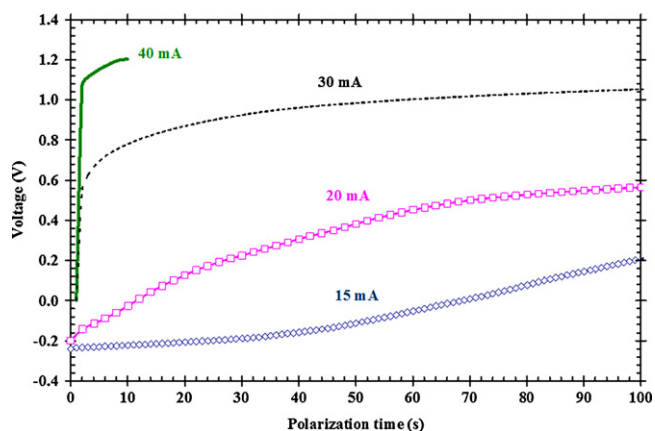
Fig. 5. Polarization curves of a 0.02 g mL^{-1} coal slurry solution with 4 M H$_2$SO$_4$ as the electrolyte at different currents (15, 20, 30 and 40 mA) at 108 °C. Coal slurry solutions cannot support currents higher than 40 mA.
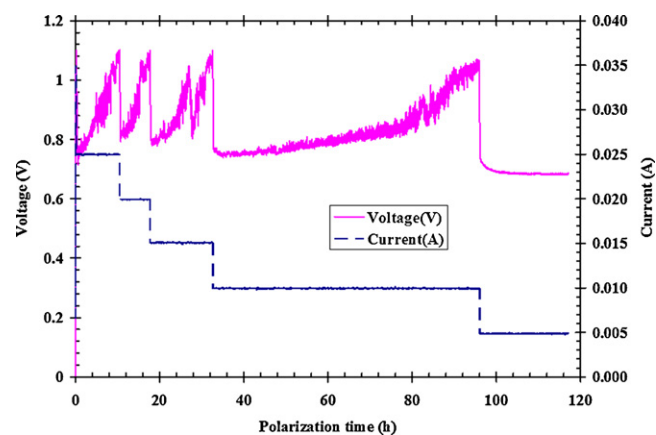
Fig. 6. Polarization curve for the 0.02 g mL^{-1} coal slurry solution with 4 M H$_2$SO$_4$ as the electrolyte under the currents ranging from 35 to 5 mA at 108 °C. The results show that small amount of coal was oxidized at currents higher than 25 mA, while more coal was oxidized under 25 mA.

polarization experiments. The negative cell voltages shown in the figure at 20 and 15 mA current at the initial polarization times are due to the electrode stabilization process.

Polarization experiments were carried out to a 0.02 g mL^{-1} coal slurry solution with 4 M H$_2$SO$_4$ as the electrolyte at 108 °C at different currents ranging from 35 mA to 5 mA. During the polarization, the current was first set to 35 mA, and the required cell voltage increased due to a decrease of the reactive components in the solution. When the voltage increased to 1.1 V, the current was stepped down to a lower value, and the polarization experiment continued. The procedure was repeated several times until a current of 5 mA was reached (see Fig. 6). The cell could be polarized for long times at currents under 30 mA: 10 h at 25 mA, 8 h at 20 mA, 15 h at 15 mA, 65 h at 10 mA, and much longer at 5 mA.

These results justified that coal slurry solution without adding any other additive such as iron can be oxidized and the most reactive components are oxidized at higher currents, and the less reactive components are oxidized at lower currents. The iron concentration was analyzed for the original coal slurry solution and the results (Table 2, experiment IV) show that about 2 mM Fe(II) and 2 mM Fe(III) were found in the coal slurry solution. After the polarization experiments, most of the Fe(II) was oxidized to Fe(III) ions. The coal Faradaic efficiency was 91.15%, which means 91.15% hydrogen gas produced was attributed to coal oxidation, while only 8.85% hydrogen gas was attributed to the Fe(II) ions, which were leached out from the original coal slurry solution.

The gas analysis from the anodic and cathodic reservoirs is shown in Table 4. The concentration of hydrogen and CO$_2$ increased at both anode and cathode sides along with the polarization time. It was found that H$_2$ was detected at the anode side and trace CO$_2$ was detected at the cathode side. A possible explanation for this result is that H$_2$ permeated from the cathode side due to the concentration difference between the cathode and anode side, similar for the CO$_2$ in the cathodic side. Analysis in the gas collector justified this explanation, no H$_2$ was found in the anode gas collector and no CO$_2$ was found in the cathode gas collector. In addition, the gas analysis results show that trace CO was only detected at short polarization times, and no CO was detected after long polarization times. This indicates that CO is not the final oxidation product of coal electro-oxidation.

3.5. Polarization experiments on extracted and residual solutions

As shown in section 3.4, about 2 mM Fe(II) and Fe(III) exist in the original coal slurry solution. In order to determine if the oxidation

Table 4
Gas concentration changes during the polarization of the original coal slurry solution.

	Time (h)	H_2 (%)	O_2 (%)	N_2 (%)	CO (%)	CO_2 (%)
Original coal/anode (in reservoir)	2	5.69	26.06	68.22	0.00	0.03
	6	43.19	8.27	47.10	0.02	1.42
	7	41.49	8.38	47.80	0.00	2.33
	20	42.82	7.57	47.21	0.00	2.40
	35	44.35	6.10	46.79	0.00	2.76
	45	52.25	6.50	38.45	0.00	2.80
	80	54.01	5.91	37.21	0.00	2.87
	95	55.92	5.19	35.88	0.00	3.01
Original coal/anode (gas collector)	95	0.00	28.72	70.85	0.00	0.43
Original coal/cathode (in reservoir)	6	88.94	4.47	6.57	0.00	0.02
	20	90.69	3.09	6.20	0.00	0.02
	35	92.36	2.54	5.08	0.00	0.02
	45	93.26	2.24	4.48	0.00	0.02
	80	93.39	2.20	4.40	0.00	0.01
	95	94.57	1.81	3.61	0.00	0.01
Original coal/cathode (gas collector)	95	62.32	10.79	26.89	0.00	0.00

of coal at low currents is related to the trace iron ions in the solution or not, coal particles were filtered out of the coal slurry solution. The procedure was the same as that reported in Section 3.2. The extracted solution contains all the components leached out from the coal (through the filter). The filtered coal particles collected were mixed with 4 M H_2SO_4 and this solution was called residual solution.

Polarization experiments were carried out for the extracted solution described above, the applied current was progressively stepped down from 35 to 5 mA, the results are shown in Fig. 7. The concentration of iron ions during the polarization was measured, and the results are recorded in Table 2, experiment V. Short polarization times were observed for the extracted solution. The experiments stopped as soon as all Fe(II) ions were oxidized to Fe(III). The results indicate that no reactive components were leached out from the coal slurry solution, except for the iron ions. Compared with the conclusions of previous authors [10,11], our results indicate that cyclic voltammetry analysis determines the oxidation of Fe(II) ions only. In addition, there is no contact between the coal particles and the electrode in unstirred solutions. Therefore, it is not appropriate to study the kinetics of coal slurries by using cyclic voltammetry techniques.

An interesting finding is that the polarization time at 35 mA of original coal slurry solution is shorter than that of the extracted solution (Table 2, experiments IV and V). The iron ions concentrations are the same in both solutions, with the existence of coal

oxidation, the original coal solution should perform better. A possible reason for this phenomenon is that the Fe(II) ions and coal particles with adsorbed Fe(III) compete for the electrode surface, but Fe(II) oxidation is faster than coal oxidation, then the solution that only contain iron ions can sustain higher currents than the solution containing coal particles.

Polarization experiments were carried out for the residual solution at different currents ranging from 35 to 5 mA, see Fig. 8. Iron concentration analysis (Table 2, experiment VI) shows that there were no iron ions in the filtered coal solution before and after the polarization experiments, which validates the extracting procedure. The polarization only lasted several minutes, which indicates that pure coal particles without any iron ions cannot be oxidized at a cell potential below 1.1 V. This result demonstrates the catalytic effect of the iron ions (or some other dissolved components from the coal) on the electro-oxidation of coal.

### 3.6. Effect of Fe(II) and Fe(III) separately

In order to further demonstrate the iron ion effect, a small amount of iron salts was added to the residual slurry solution such that the concentration would be 8 mM Fe(II) and 8 mM Fe(III). Polarization tests were performed in the solution at currents ranging from 35 to 10 mA, see Fig. 9. The results indicate that the iron ions added to the solution cause the oxidation of coal. This justifies the assumption that iron ions in the solution take a role on the electro-
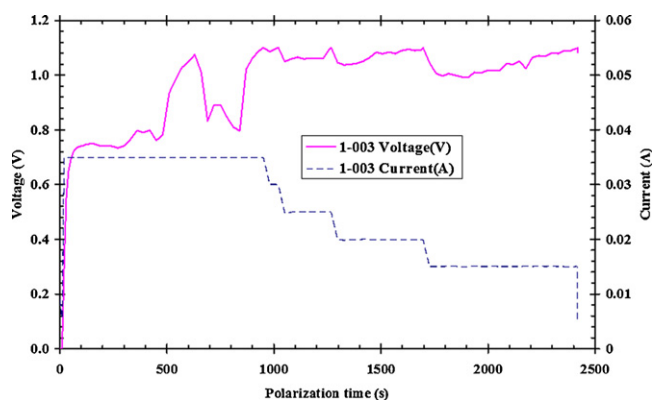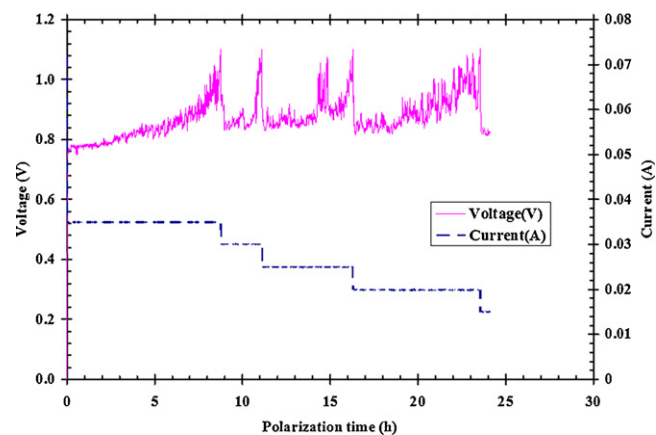

Fig. 7. Polarization curves of the extracted solution (4 M H_2SO_4 as the electrolyte, applied current ranging from 35 to 15 mA, and operating temperature 108 °C). The results indicate that the polarization experiment on the extracted solution can only last short time and the time is consistent with the iron ion changes in the solution.
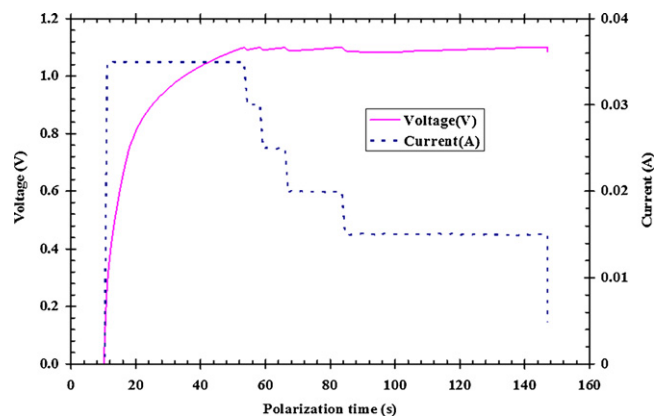
Fig. 8. Polarization curve of the residual solution (4 M H_2SO_4 as the electrolyte, applied currents ranging from 35 to 15 mA, and operating temperature 108 °C). It indicates that coal particles without any additives (e.g., added iron) cannot be oxidized.
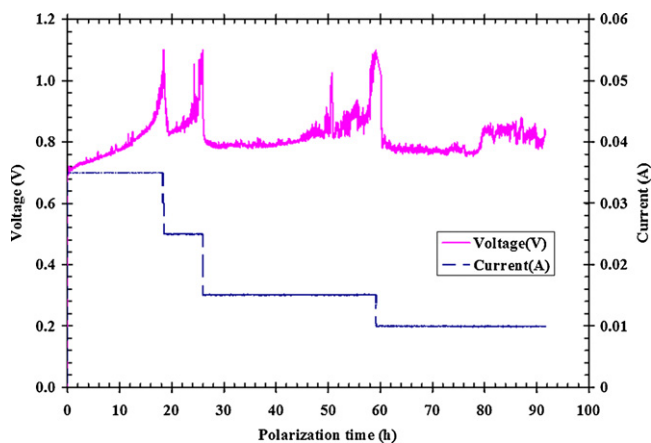
Fig. 9. Polarization curves of the $0.02\,g\,mL^{-1}$ coal slurry solution ($4\,M\,H_2SO_4$ as the electrolyte, additional 8 mM Fe(II) and 8 mM Fe(III)) at currents ranging from 35 to 10 mA, and operating temperature of 108 °C. The results show that small amount of iron ions can cause the coal oxidation at higher current.


Fig. 10. Polarization curves of the $0.02\,g\,mL^{-1}$ coal slurry solution ($4\,M\,H_2SO_4$ as the electrolyte, additional 16 mM Fe(III)) at currents ranging from 35 to 20 mA, and operating temperature of 108 °C. The results show that coal was oxidized by Fe(III) at 35 mA and lower currents, and it indicates the catalytic effect of Fe(III) on coal oxidation.

oxidation of coal. The concentration of 8 mM of iron ions is higher than that in the original coal (see experiment IV, Table 2), and then the solution can be polarized at 35 mA for a longer time, which indicates that more coal was oxidized than in the original coal oxidation solution. In addition, the changes in the iron ion concentration after electrolysis (see Table 2, experiment VII) indicate that most Fe(II) was oxidized to Fe(III), however, 2 mM Fe(II) was still detected in the final solution after electrolysis. This finding shows that Fe(II)

concentration is not the limiting factor for further coal oxidation. Therefore, it could be hypothesized that the low current may be due to a concentration decrease of the reactive components on the surface of the coal particles and not due to the lack of Fe(II) ions in the slurry.

Finally, the effect of Fe(II) and Fe(III) was evaluated separately. In order to separate the effect of Fe(II) and Fe(III) ions, a residual solu-
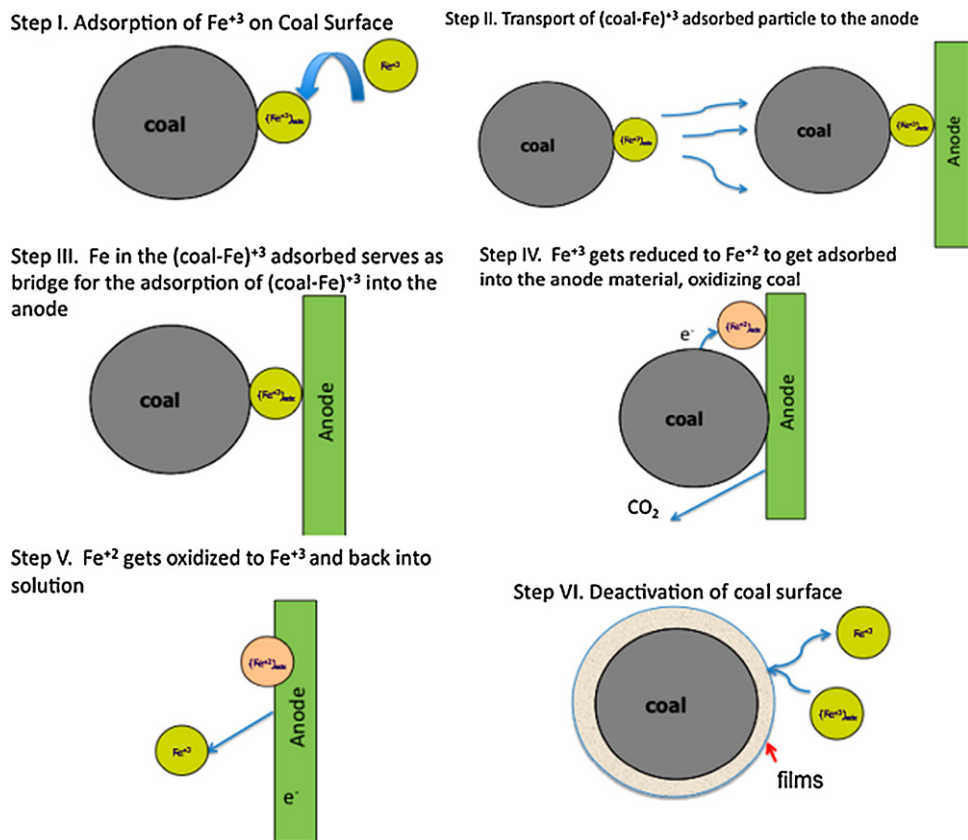
Fig. 11. Schematic representation of the proposed mechanism for the electro-oxidation of coal. The mechanism includes (I) Adsorption of Fe(III) ions on the surface of the coal particles, (II) transport of coal particles to the surface of the anode of the electrolytic cell, (III) electro-adsorption of coal particle at the surface of the anode through Fe(III) ions adsorbed at the surface of the coal, (IV) oxidation of coal to CO_2 and other high molecular weight hydrocarbons, while adsorbed Fe(III) is reduced to Fe(II) and stays adsorbed at the surface of the anode electrode, (V) oxidation of Fe(II) to Fe(III) ions, regenerating the concentration of Fe(III) in the system, and (VI) passivation of the coal due to the growth of films at the surface of the particle. The films may prevent the adsorption of Fe(III) ions into the coal particle and/or increase the stability of Fe(III) adsorbed which prevents the electro-oxidation at the surface of the anode.

tion with 16 mM Fe(III) ions was tested, and the results are shown in Fig. 10. The changes in the iron ion concentration (see Table 2, experiment VIII) show that about 2 mM Fe(II) was detected after the polarization experiments, which was not present before polarization. This result confirms that Fe(III) ions were reduced back to Fe(II) ions during coal oxidation. It was also found that the solution containing only Fe(III) ions could sustain the coal oxidation at the applied current load (between 35 and 5 mA) for a significant long time (up to 25 h) as shown in Fig. 10. The results demonstrate that Fe(III) ions participate in the electrochemical oxidation of coal and that coal oxidation can take place without Fe(II) ions present originally in the slurry. In addition, the reduction rate of Fe(III) ions seems to be fast enough to provide sufficient Fe(II) ions to sustain a 35 mA oxidation current.

However, the coal conversion to carbon dioxide is still low (3.5% considering the results shown in Table 4) at the operating conditions used in this study. A possible explanation is that the polarization is blocked by the growth of films on the surface of the coal particles, and the films prevent the active sites of the coal to react on the electrode as reported in the literature [13,17]. De Abreu et al. [17] performed a through characterization of the films that grow at the surface of the coal particles using different techniques including XPS and EDX. Illite, siderite, and carbonate films were identified after electrolysis. More studies on the film (preferable with a redesign of the electrolytic cell to observe *in situ* film formation) could help to provide a better understanding of the reaction mechanisms and further increase the coal conversion rate.

3.7. Proposed mechanism

From the above results, it can be concluded that coal oxidation takes place on the surface of the electrode with the aid of Fe(III) ions. According to this conclusion, one possible mechanism is proposed for coal electro-oxidation. The mechanism includes six steps, which are described below (see Fig. 11):

a. Step I: Fe(III) ions in solution are adsorbed on the surface of a coal particle.
b. Step II: The adsorbed $(C–Fe(III))_{ads}$ structure flows towards the surface of the electrode due to forced flow.
c. Step III: It is hypothesized that when the $(C–Fe(III))_{ads}$ structure is in contact with the anode electrode, $Fe(III)_{ads}$ on the coal acts as a bridge between the coal and the electrode.
d. Step IV: It is possible that due to steric effects and/or electrostatic charges, Fe(III) will get de-adsorbed from the coal particle to the anode electrode, and then the oxidation of coal takes place, simultaneously reducing Fe(III) to Fe(II). During the process coal can be oxidized to CO_2 and/or other large chain hydrocarbons.
e. Step V: The Fe(II) ions can be oxidized at the anode of the electrolytic cell to regenerate Fe(III) ions.
f. Step VI: As coal oxidizes, films grow on the surface of the coal particle preventing the oxidation of coal as reported in the literature [13,17]. It is hypothesized that the films may prevent the adsorption of Fe(III) ions into the surface of the coal particle (bouncing back to the solution as shown in Fig. 11). Another possibility is that the films and adsorbed Fe(III) ions form complex stable structures that prevent the oxidation of coal.

The proposed mechanism includes the complicated reactions between coal particles and Fe(III) on the surface of the electrode (step IV), which is not clear yet. In order to further validate the mechanism, additional analysis of the cell reactions is needed, which will require modifying the experimental setup used in this paper.

3.8. Conclusions

The kinetics of coal electrolysis was studied on a bench continuous coal electrolytic cell setup at intermediate temperatures. The experimental results indicate that coal oxidation is an electro-oxidation process; the coal particles are the major reaction components, and the reaction takes place through the contact between the coal particles and the electrode. The effect of iron ions on coal oxidation demonstrated that small amounts of iron ions can initiate the coal oxidation, and that Fe(III) plays a catalytic role in coal oxidation. At high applied currents the oxidation of coal by Fe(III) is the limiting factor. The oxidation experiments at low applied currents showed that coal oxidation by Fe(III) is not the limiting step at the operating conditions described in this paper, while it is proposed that the films formed on the surface of the coal particles prevent the further oxidation of coal.

Based on the results obtained, a mechanism was proposed to describe the coal oxidation process, which is directly related to the surface characteristics of coal particles, electrode catalysts, and the presence of Fe(III) ions. Further studies on the kinetics require a new experimental setup, which could provide the *in situ* information of the cell reaction. In addition, higher operating temperatures in the cell, or the use of a solvent to dissolve the films on the surface of the coal may help increasing the coal conversion rate.

Acknowledgements

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