

The electrochemical production of hydrogen using a carbonaceous fuel as an anode depolarizer

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Carbon depolarized water electrolysis using the ferrous/ferric redox cycle as a mediator is discussed. Complete combustion of non-cellulosic fuels by this process is not a realistic goal, though substantial voltage reduction over conventional water electrolysis can be achieved and unique by-product materials of possible upgraded value over feedstocks are produced.

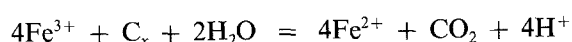
1. Introduction

Reducing the costs of electrolytic hydrogen production may become of increasing importance if the cost of fossil fuels escalates significantly. Herein we examine an alternative to conventional electrolytic means of hydrogen production and steam reforming of carbonaceous substances. Our work was inspired by the attempts of Coughlin *et al.* [1, 2] to use coal as a fuel at the anode of an electrolytic hydrogen generator. Theoretically, the electrode potential required for this step is much less than that required to evolve oxygen.

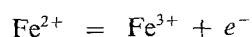
The central questions lie in what reaction rate and fuel utilization are possible. Coughlin's work produced unacceptably low rates. At the temperatures used, only very low current density (of the order 5–10 mA cm⁻²) could be sustained before the electrode potential climbed to that expected for oxygen evolution.

Acidic aqueous solutions of ferric ions can rapidly oxidize slurries of carbon itself and carbonaceous materials at elevated temperature and pressure. The reaction is of interest as it offers a catalytically assisted method to replace oxygen evolution with the less energy intensive (i.e. lower electrode potential) indirect oxidation of carbon [3–7]. Ferric ion may be regenerated from ferrous ion with the evolution of hydrogen at practical rates in a coupled system if a proper temperature is selected so as to assure that the rates of the chemical oxidation of carbon and the electrolytic catalyst regeneration reaction are matched. These reactions are given by the following equations:

Anolyte chemical reaction

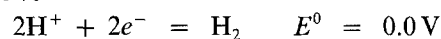


Anode reaction

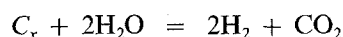


$$E^0 = +0.77 \text{ V (uncomplexed)}$$

Cathode reaction



Summed reaction (if to completion)



2. The rationale for iron as mediator

To couple an indirect aqueous oxidation of carbonaceous substances to electrolytic hydrogen production, the mediator selected must be able to accomplish the following: (1) oxidize carbon itself and its surface functional groups; (2) anodically regenerate to its higher oxidation state without parasitic oxygen evolution; (3) maintain a high solubility at high temperature in mixed sulphuric acid and carboxylic acids; (4) have an anionic-complexed state to avoid parasitic cathodic reactions in ion exchange membrane separated cells (preferably, such complexation would also lower the redox potential of the couple).

Of the ten or so redox couples that may be examined, the ferrous/ferric system best satisfies all requirements. Sulphuric acid is a natural choice of electrolyte in that much of the high sulphur content of low-cost fuel materials oxidizes to sulphate [8]. In order to avoid mixed electrolytes, the use of sulphuric acid is essential. Both ferric and ferrous sulphate are adequately soluble in sulphuric acid (this is not the case in other electrolytes that could be considered 'practical'). Two additional considerations are important: (1) at temperatures over 100°C, the solubility of the ferrous and ferric salts decreases with increased temperature [9, 10] and (2) the solubility of these salts goes through a maximum between 0.5 M and 2.0 M sulphuric acid over the temperature range 75–200°C [9, 10]. These considerations define a working range for the potential process and have provided a useful experimental guide despite uncertainties over solubility in the presence of the mixed carboxylic and humic acids that are the products of reaction.

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3. The observed rate laws for ferric ion oxidation of carbonaceous substances

The kinetics of the chemical oxidation process were studied to determine parameters for coupling the process to a hydrogen-producing, ferric-regenerating electrochemical cell.

The kinetics of the ferric ion oxidation of the surface of ground coal were measured as a function of iron concentration, carbon content in the slurries and sulphuric acid concentration. It is important to emphasize that the following results are for freshly prepared coal surfaces. The rate laws are obeyed as more and more of the surface becomes covered with slowly decarboxylating functionality; however, the observed rate constants diminish. Thus any constants determined only portray a moment in time because the chemical nature of the carbon surface is constantly changing. Remarkable consistency in the reaction orders was found for a process that must necessarily be a collection of a multitude of parallel and sequential oxidations.

The kinetic analysis was performed on the assumption that the chemical oxidation follows a rate law of the form:

$$-1/4 \frac{d[\text{Fe}^{3+}]}{dt} = K[\text{Fe}^{3+}]^x[\text{C}]^y$$

In turn the reaction was run with varying amounts of ferric ion, carbon content and sulphuric acid. Observed rate constants (K_{obs}) were determined in each case for purposes of graphical determination of reaction orders. It is vital to note the K_{obs} values cited in the following reaction order analysis are not in each case dimensionally equal, but represent composites of the true rate constant and terms in the model law (above) held constant in each individual experiment.

The effect of ferric ion concentration is second

order, as shown by Fig. 1 for the oxidation process at 120°C. In the three experiments shown hydrogen ion and carbon were present in great excess. Calculations showed that $[\text{C}]$ and $[\text{H}^+]$ could not change meaningfully during the course of the experiments. This can be seen, recognizing that on a per litre basis approximately 27 moles of carbon, 10 moles of hydrogen ion and 0.074 moles of ferric ion are present. The data were obtained by chromium titration of aliquots withdrawn from a Teflon-lined pressure reaction vessel over intervals of time. At higher temperature, the reaction with the freshly prepared surface was too rapid for the extraction and titration technique to be possible, and thus the kinetic results reported are limited to 120°C.

With ferric ion and sulphuric acid in great excess for the reaction time selected, carbon content in the slurries affects the production of ferrous ion according to a third order rate law (Fig. 2). This was determined by plotting K_{obs} from the slopes in Fig. 1 on a log/log scale.

With ferric ion and carbon present in great excess for the reaction time selected, the effect of sulphuric acid concentration appears to follow a 3/4 order rate law (Fig. 3). As hydrogen ion is a product of reaction rather than a reactant, it is likely it acts as a catalyst for the various oxidations occurring.

A mechanism rationalizing the reaction orders observed was not discovered, however we may conclude that

$$-1/4 \frac{d[\text{Fe}^{3+}]}{dt} = K[\text{Fe}^{3+}]^2[\text{C}]^3$$

Following such a model, the true rate constant for the reaction could be obtained by integration of

$$-\int \frac{d[\text{Fe}^{3+}]}{[\text{Fe}^{3+}]^2 \left([\text{C}]_0 - \frac{[\text{Fe}^{3+}]_0}{4} + \frac{[\text{Fe}^{3+}]}{4} \right)^3} = 4Kt$$

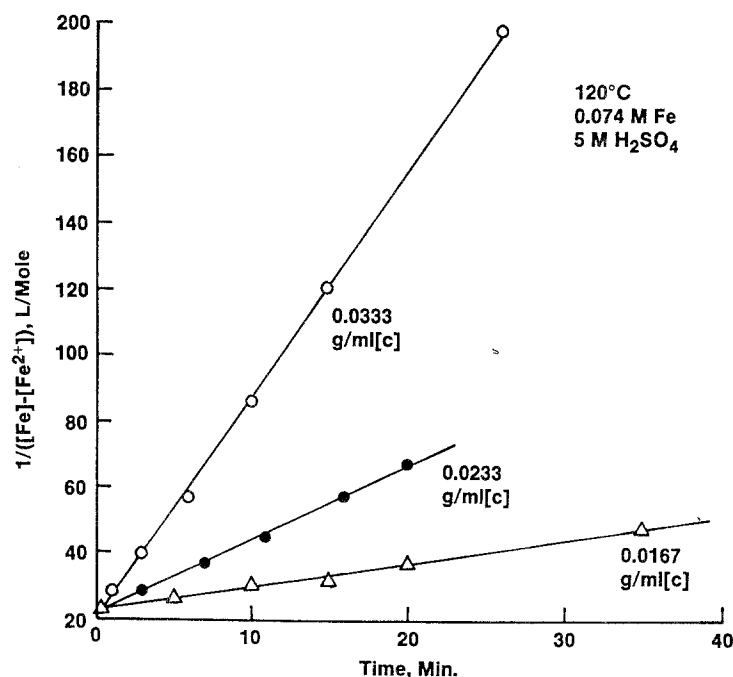


Fig. 1. The second-order kinetics of ferric oxidation of carbonaceous materials. Three carbon concentrations shown. K_{obs} is a composite term unique to this experiment.

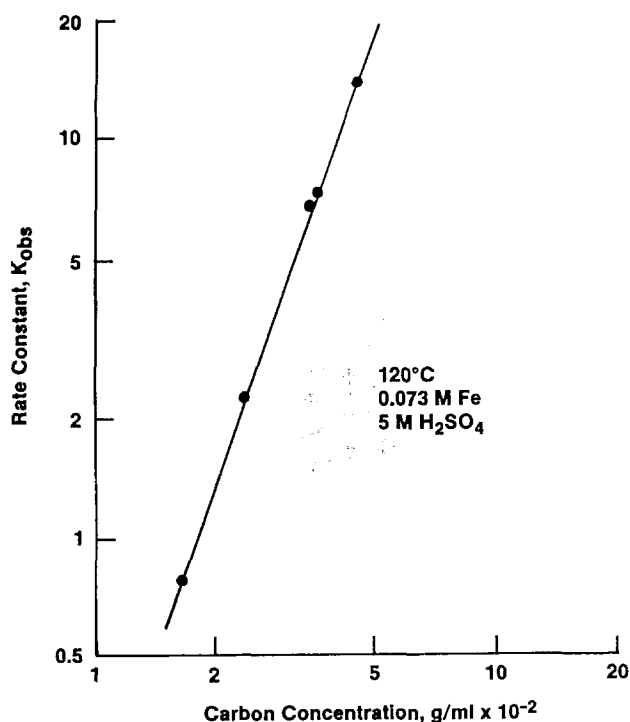


Fig. 2. The observed third-order effect of carbonaceous material concentration on the oxidation by ferric ion. K_{obs} is a composite term unique to Fig. 1 and this analysis of Fig. 1.

Bearing in mind the reactivity of the carbon surface decreases with increasing carboxylic functionality, and a complete model must include a treatment of the hydrogen ion catalysis observed, carrying forward the calculation of a true rate constant based on the above model did not appear worthwhile given its limitations.

Despite the aforementioned complexities, the overall process of ferric ion oxidation of carbonaceous substances follows the Arrhenius expression for the increased rate of reaction with increased temperature. The activation energy that can be determined from the slope in Fig. 4 is specific to the reactant concentrations given in the figure caption, and the figure is not constructed with true rate constant values. Nevertheless, Arrhenius behavior is confirmed.

Work by Kreysa and Kochanek [11] confirms the

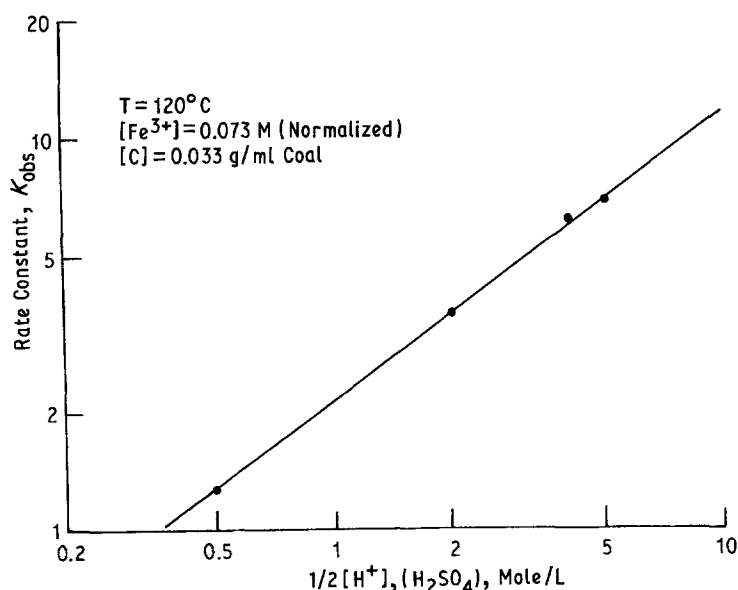


Fig. 3. The observed 3/4-order effect of hydrogen ion concentration on the oxidation of carbonaceous materials by ferric ion. K_{obs} is a composite term unique to this experiment.

second order nature of the reaction between ferric ion and coal.

4. Coupling the processes: experimental considerations

As it became clear that iron leached from fuels (or deliberately added) acted as a redox 'shuttle species', it was discovered that most carbonaceous materials from petroleum cokes and tars to wood flour and even pure graphite could be oxidized under the same conditions. One very marked difference did occur; non-aromatically based materials such as cellulose were almost completely consumed, whereas those fuels with a tendency to a graphitic structural unit, coal, coke, graphite etc., were consumed at far lower rates.

The aqueous ferric ion oxidation of carbon or carbonaceous material proceeds as long as there are sufficient surface sites of carbon or functional groups available for oxidative attack by ferric ion. The surface area of the fuel diminishes during the oxidation due to both the build-up of stable carboxylic acid functionality and the evolution of large amounts of carbon as carbon dioxide. Consequently, the availability of additional surface and the rates of decarboxylation processes become rate determining. A continuous process is possible only if additional fuel is added, enough decarboxylation is achieved and reaction products are removed.

The operation of a process requiring input of electricity that does not take advantage of all available carbonaceous energy has two obvious constraints: (1) the fuel must be very inexpensive (e.g. high-sulphur petroleum coke) and (2) the by-products of reaction should have some possibly upgraded value over the starting fuel.

The by-products of reaction are soluble thermally stable low molecular weight humic and fulvic acid substances and heavily carboxylated carbon fines. Rather than simply optimizing such a process in terms of voltage savings, the values of these by-products in necessarily commodity applications determine the optimal product mix for the process and, in essence, are the prime determining factors in selecting process operating

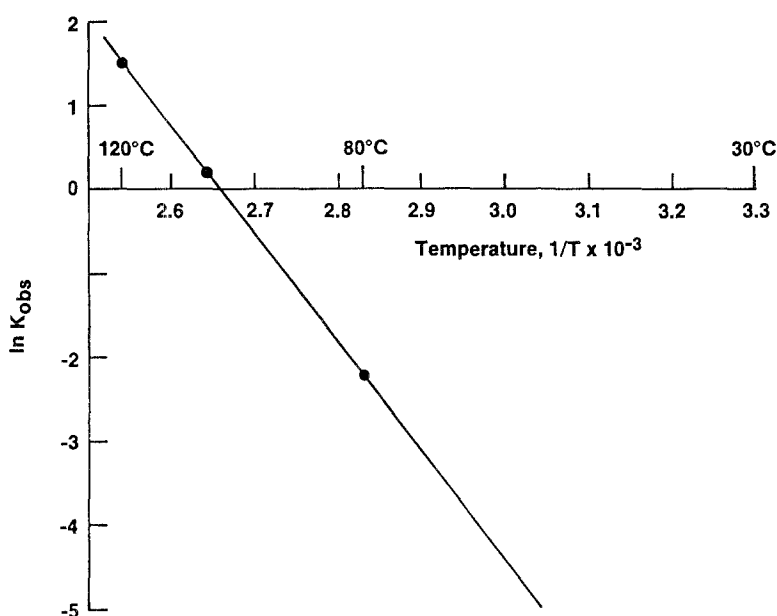


Fig. 4. The Arrhenius dependence of the ferric oxidation of carbonaceous materials. Concentrations: 0.073 M ferric ion, 333 g l⁻¹ carbon, 0.5 M sulphuric acid.

parameters. There will be a voltage savings over conventional water electrolysis with this process, but with the operating parameters selected by the desired mix of by-products, the voltage savings will not likely be as large as possible.

Two distinct methods of operating carbon depolarized water electrolysis were shown to be possible. Either a slurry of particulates can be circulated through the electrochemical cells or a separate 'digestion' bed can be coupled to the cells using filtration such that only clarified ferrous-bearing electrolyte is circulated to the cells. The advantage in circulating particulates of carbon is improved iron mass transport; but it is felt this is offset by considerations of pumping, blockages and solid by-products removal.

Dimensionally stable anode-type materials were used as anodes and proved stable to corrosion processes within the range of sub-oxygen evolution anode potentials employed. These materials were ruthenium dioxide/titanium dioxide coatings on titanium substrates. In experimental trials using concentrations of sulphuric acid 5 M and greater, corrosion of the titanium substrate became severe at 140°C operating temperatures and above. At the 0.5 M sulphuric acid concentration chosen for the bulk of the work, titanium corrosion was not evident to visual inspection at 180°C.

Stainless steel cathodes were employed and performed satisfactorily given the cathodic protection high-rate hydrogen evolution imparts. Their open circuit corrosion at high temperature was not investigated.

The electrochemical cells were divided with Teflon-reinforced Nafion membranes. Nafion experienced a bleaching indicative of some long-term effects of the environment of the cells. The purpose of the membrane was to restrict anionically complexed iron and carboxylic acid oxidation products to the anode compartment as much as possible. Parasitic reductions were thus reduced. Several elementary acids such as acetic acid, oxalic acid and propionic acid were extracted

from steady-state anolyte with tributylphosphate and confirmed by gas chromatography.

Electrochemical cells and digestion apparatus were constructed from Teflon- or rulon-lined steel pressure vessels. The high temperature oxidizing environment prohibited the use of most other materials of construction.

In all cells, cathodic hydrogen and anodic carbon dioxide were taken in a combined product stream to either analysis or disposal. Neither hydrogen sulphide or sulphur dioxide were detected in the product gases; however, neither can all of the sulphur content be converted to sulphate via ferric oxidation [9, 12].

Saturated calomel (SCE) reference electrodes were used to monitor electrode potentials. These were arranged externally and used at ambient temperature and pressure, the connection to the electrolyte of the cell being made through a thick porous Teflon plug that restricted cell-to-reference chamber leakage to minimal levels. Temperature corrections are available in the literature [13].

Coal or high-sulphur petroleum coke (ground to 80% below 100 mesh) were used as fuel materials. Due to the slight density differential between the electrolyte and the carbonaceous material, complete fluidization could be achieved (even by magnetic stirring) up to 0.4 kg fuel l⁻¹ electrolyte.

Two cell types were used in this study: (1) concentric mesh electrodes wherein fluidization in the central anode compartment was achieved by magnetic stirring and (2) parallel planar electrodes mounted in a flow channel, the anode compartment either fed with a pumped particulate slurry or fed with clarified ferrous-bearing electrolyte from a separate digestion reactor.

5. Performance of carbon-depolarized water electrolysis

Figure 5 presents an experiment examining the effect of iron redox catalysis on carbon depolarization in

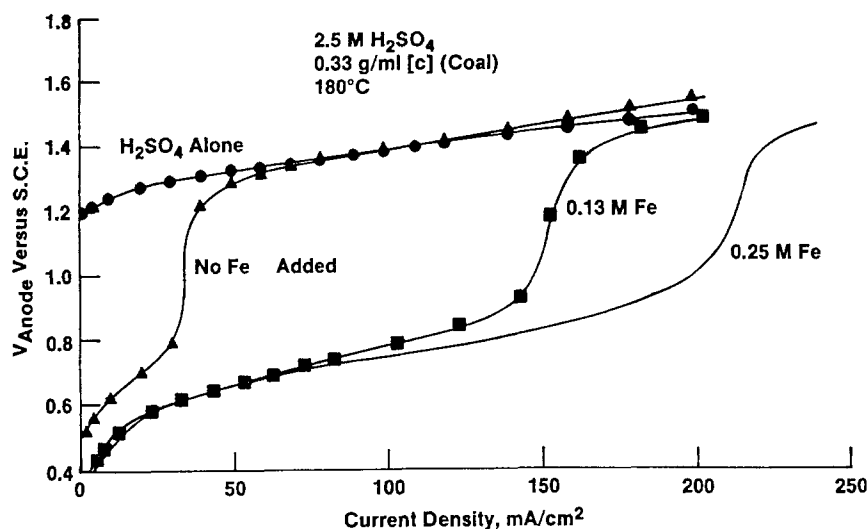


Fig. 5. Anodic polarization curves depicting carbon depolarization and the catalytic effect of iron thereon.

water electrolysis. Sulphuric acid alone is electrolyzed producing a baseline anode potential for comparison to oxygen evolution. Next, a 0.33 kg l⁻¹ 100-mesh coal slurry is electrolyzed. Some depolarization is to be noted, producing a limiting current behavior at 30 mA cm⁻² under the specific conditions of this fluidization by magnetic stirring. This is the type of carbon depolarization noted by Coughlin [1, 2]. The current density here is somewhat higher than he reported primarily due to the higher (180°C, 150 psi) temperature conditions. In this process, current is attributable to the anodic oxidation of surface functionality produced either through contact with the anode or through leaching of iron naturally contained within the fuel material [14].

Two progressive additions of ferric ion were made and are also plotted in Fig. 5. Depolarization of approximately 600 mV is seen extending to limiting currents of 150 mA cm⁻² and 200 mA cm⁻² depending on the iron concentrations present. These depolarizations are not maintained throughout the combustion

of the fuel materials, as will be noted in subsequent discussion.

Over time, 100-mesh delayed petroleum coke has been taken to a maximum of 78% by weight 'depth of combustion' in 0.5 M sulphuric acid electrolyte containing 0.5 M total iron at 180°C. (The 'depth of combustion' is calculated from the current theoretically required to combust the starting elemental analysis totally to carbon dioxide, sulphuric acid and water.) Coal and wood flour behave similarly. Current densities depend on the comparative sizes of the fuel digestion bed and the electrochemical ferric ion regeneration component, but have been sustained to 50% depth of combustion at over 250 mA cm⁻² under the above conditions using a slurry electrolyte with an initial concentration of 0.4 kg l⁻¹ petroleum coke.

The mechanism of the effect of iron was clarified in the experiment of Fig. 6, in which cerium(IV) was titrated into a cell operating at steady state. The current passed dropped off dramatically as all available ferrous ion was converted to ferric. Current recovered

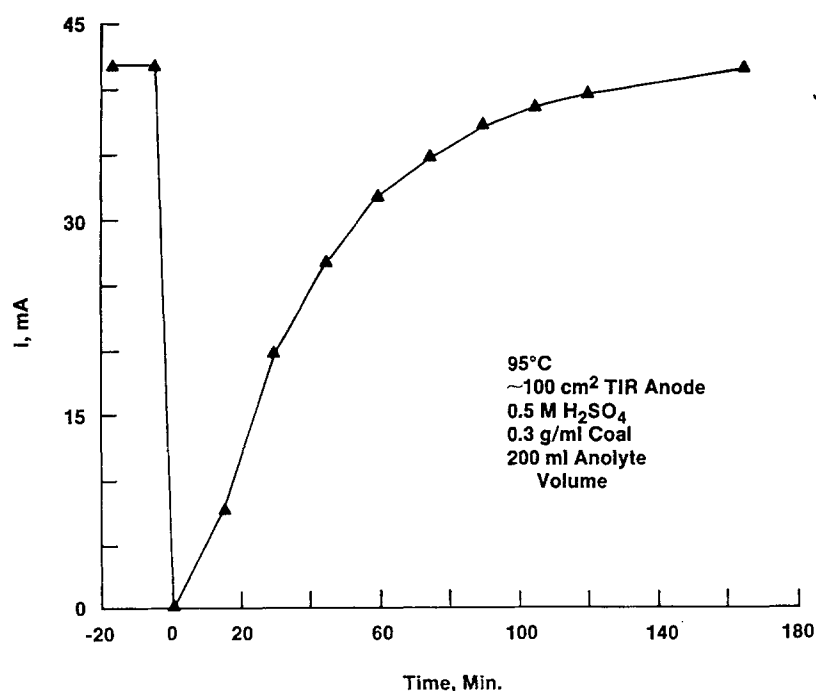


Fig. 6. The regeneration of the ferrous current carrier subsequent to cerium(IV) titration.

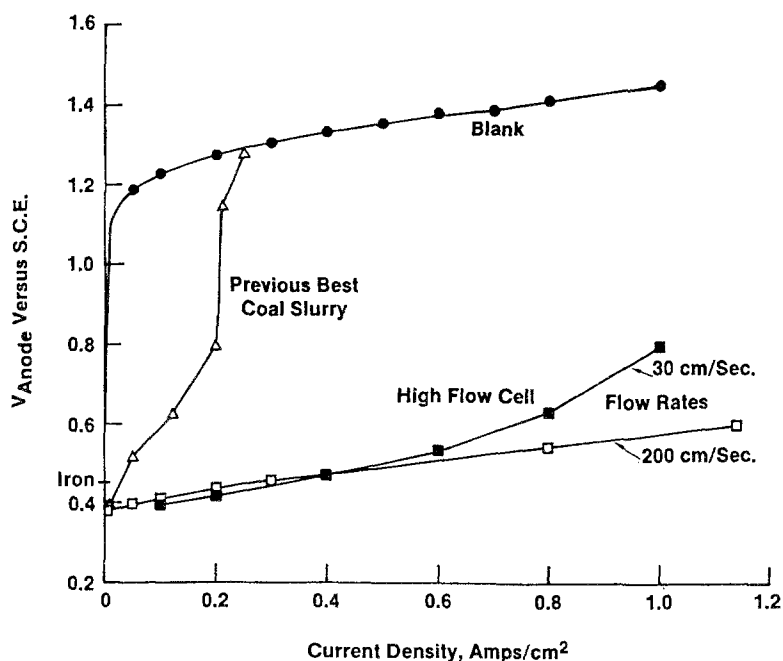


Fig. 7. Anodic polarization curves for clarified electrolytes in a parallel-plate flow channel cell.

as additional ferrous ion was produced through the oxidation of the carbonaceous fuel material. (Cerium(III) could not reoxidize at the potential of 0.65 V vs SCE.)

Limiting currents for the anodic oxidation of ferrous ion derived from carbonaceous fuel can be much higher than illustrated in Fig. 5. Figure 7 presents polarization curves in parallel-plate cell geometry at high electrolyte flow rates. Flow rates of 0.030–0.200 m s⁻¹ of clarified electrolyte from a digestion bed were pumped through this cell that had a gap between anode and membrane of 0.004 m. The experiment confirmed that appreciable current densities were possible with electrolytes of 0.5 M total iron dissolved in 0.5 M sulphuric acid systems when operated at high temperature. As before, these data were taken with freshly ground fuel materials and are not reflective of all depths of combustion.

As the fuel material is combusted (whether it is petroleum coke, coal, cellulose, etc.), its surface builds

up carboxylic acid functionality. At the temperatures selected, much of this coverage undergoes thermal and/or oxidative decarboxylation, producing carbon dioxide. Such decarboxylation reactions are known to be slow. After extended operation, therefore, fuel surfaces become ‘passivated’, that is, left with the most stable carboxylic acid structures.

Figure 8 shows that high current densities in constant current electrolysis can be sustained for shorter periods of time than can lower current densities. (In these experiments a voltage limit was used when the anode potential climbed to 0.80 V vs SCE — the start of a region where the depolarization process could end, and oxygen evolution could begin, whereupon constant current control was terminated.) Decarboxylation of the heavily carboxylated surface cannot be maintained at the higher rates of anodic oxidation, ultimately forcing a reduction of the rate of ferric ion regeneration. Low current densities ultimately achieve greater depths of combustion of the fuel.

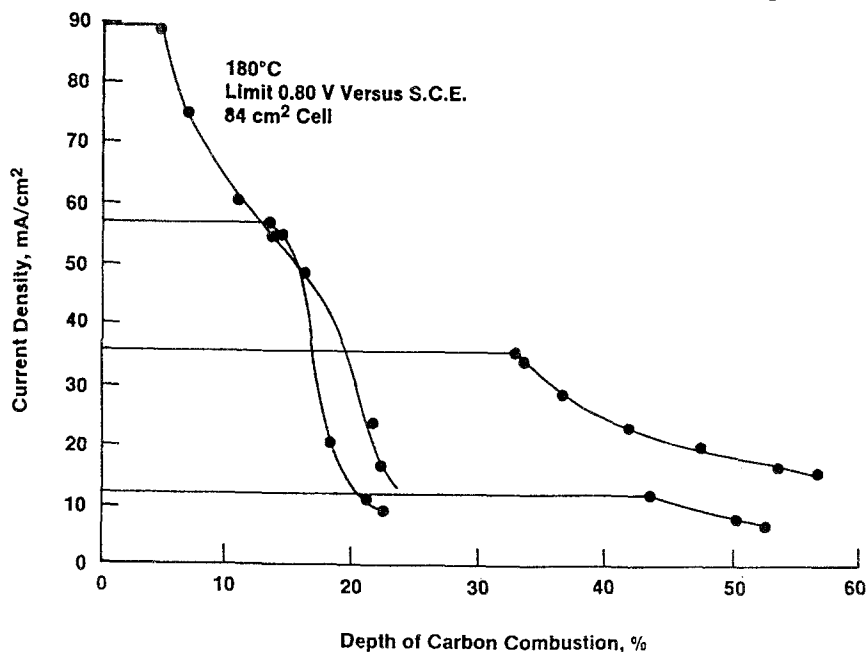


Fig. 8. The relationship between ferrous/ferric recycle current density and the depth of combustion of fuel materials. Constant current electrolysis until an anode potential of 0.80 V vs SCE is reached.

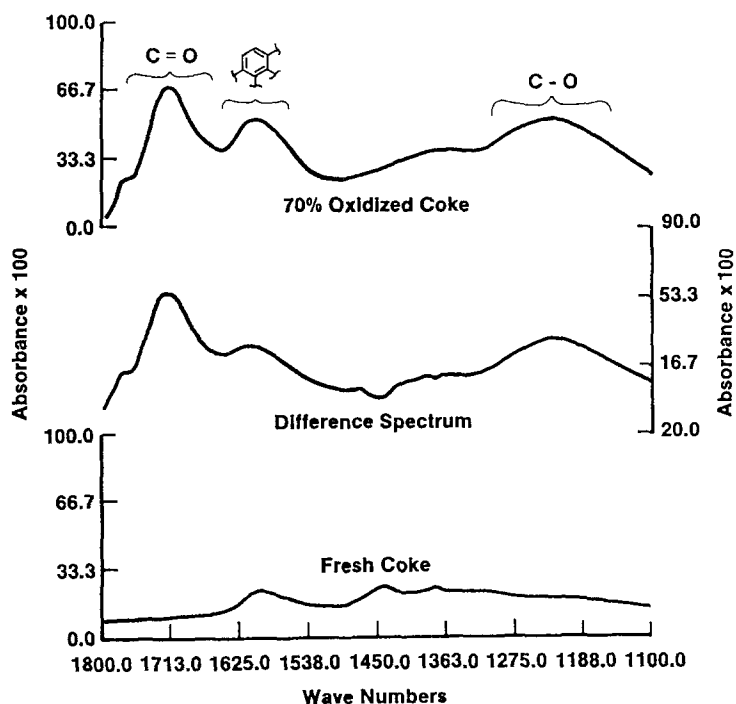


Fig. 9. Infrared verification of the addition of carboxylic functionality to fuel material surfaces.

6. Products of the oxidation

The oxidizing environment of the cells is so severe that nearly all carbonaceous materials are degraded. This leads us to conclude that such an oxidation process can possibly be of use for disposal of aqueous hazardous wastes adsorbed on fuels.

It has been confirmed through infrared spectra that the surface of any carbonaceous fuel material accumulates carboxylic acid functionality. The infrared spectra of freshly ground and 70% oxidized petroleum coke are compared in Fig. 9. Neutron activation analysis of these 70% combusted solids indicates an oxygen content of approximately 30% by weight. This represents an average of two oxygens for every five carbons.

Figure 10 shows the first order kinetics of the

aqueous thermal decarboxylation of a 50% oxidized coal sample. Oxygen contents of 25% by weight have survived treatments in 0.5 M sulphuric acid of up to 8 h at 220°C. At such slow rates of decarboxylation, systems that completely consume fuel materials cannot be designed at what we consider practical temperatures and pressures. Requirements for frequent iron recycle complicate the notion of running digestion apparatus at higher temperatures and pressures than the electrochemical apparatus. Very large iron inventories would be needed to reduce recycle requirements to a level where this could be contemplated.

Using a wet test meter, carbon dioxide evolution was monitored as a function of depth of combustion in the experiment of Fig. 11. The amount of carbon dioxide evolved from the cell is plotted in proportion

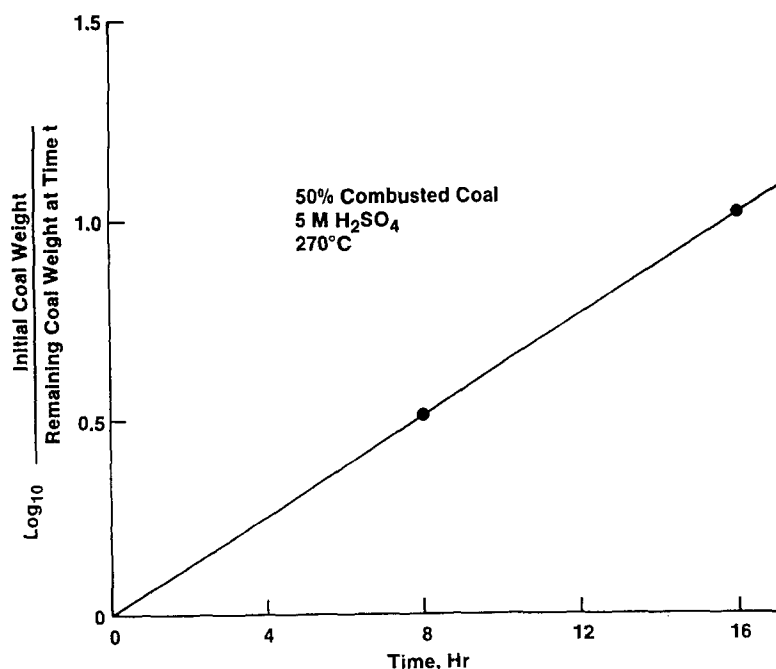


Fig. 10. The first-order aqueous decarboxylation of 50% combusted coal samples.

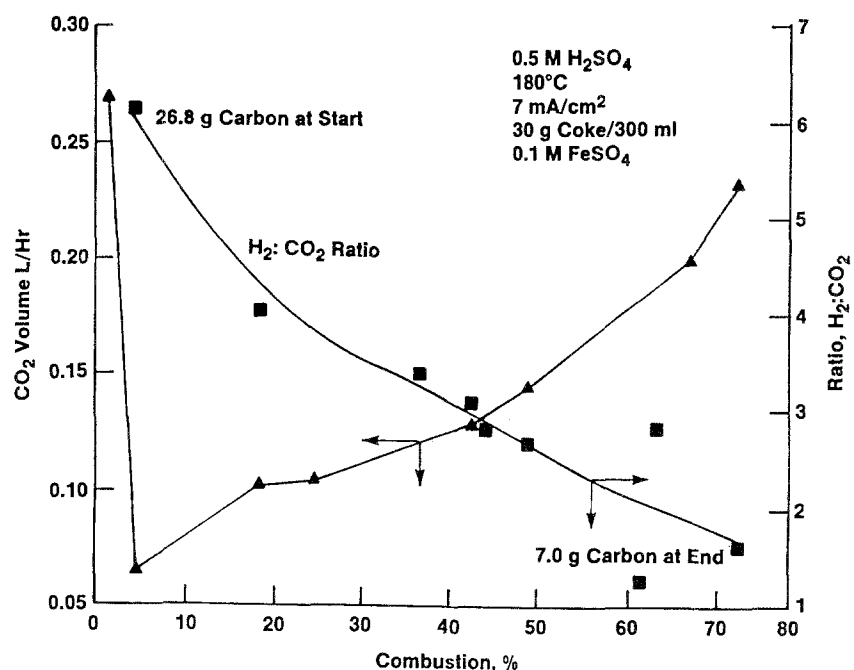


Fig. 11. The ratio of hydrogen to carbon dioxide production over the course of the oxidation of petroleum coke.

to the amount of cathodic hydrogen. For pure carbon fuels the ratio is theoretically 1:2 if all carbon is converted directly to carbon dioxide. Petroleum coke was used in the experiment of Fig. 11; due to its elemental analysis it would not be expected to combust at a ratio of 1:2, but the time dependence of carbon dioxide evolution is noteworthy. Initially, a great deal of carbon dioxide is evolved, presumably due to rapid decarboxylation of existing surface functionality. As the reaction proceeds to higher depths of combustion, less carbon dioxide is evolved as decarboxylation slows. Toward the end (in this trial, 70% depth of combustion), less carbon dioxide is evolved because the surface has accumulated groups of the greatest thermal and oxidative stability throughout the course of the reaction.

Thus, along with cathodic hydrogen and anodic carbon dioxide, two classes of by-product result: (1) heavily surface-oxidized, thermally stable carbonaceous solids of somewhat finer particle size than the starting feedstock and (2) soluble low-molecular-weight elementary and humic acids of thermal stability comparable to the solid residuum.

Even should complete fuel utilization have proved possible at perhaps a temperature of, say, 250°C, the incentive to perform such a process based on voltage savings over conventional water electrolysis would be tenuous. The thermodynamic requirements for electrolytic water decomposition decrease as temperature is raised (due to the negative $T\Delta S$). More and more heat from the environment is utilized. The opposite is true of a ferrous/ferric hydrogen-evolving cell. Electrical input requirements rise with increasing temperature (though $T\Delta S$ is negative, changes in ΔH are offsetting). At approximately 250°C, the electrical energy needs of both processes (based on full-cell decomposition potentials) are identical if overvoltage requirements are ignored. This is indicated in Fig. 12.

It is of interest then to examine the incentives for development of a process tuned not to fully combust

its carbonaceous feedstock, but rather to upgrade the value of its feed while considering hydrogen as a by-product. At the present \$35 ton⁻¹ for high-sulphur (6–8%) petroleum coke (now largely an export fuel), there may be some opportunity. Grinding costs to 100-mesh are presently of the order of \$3 ton⁻¹.

The soluble humic acids produced in the electrolyte (and by caustic washing of the solid residuum) have been shown by elemental analysis to be essentially identical to those commercially produced by the nitric acid oxidation of lignite. Applications for humic acids have been slow to develop but do include the following: soil and fertilizer additives for improved wetting [15], root initiation [16] and nitrogen retention [17], additives to drilling muds to replace more expensive and less thermally stable surfactants [18] and precursors of resins for plywood bonding [19, 20].

The highly carboxylated carbon fines are unique materials having fixed surface acidity (which are even more strongly fixed subsequent to a caustic wash). They could be used in water treatment applications, being analogous to activated carbon and other more expensive ion exchangers. It is also

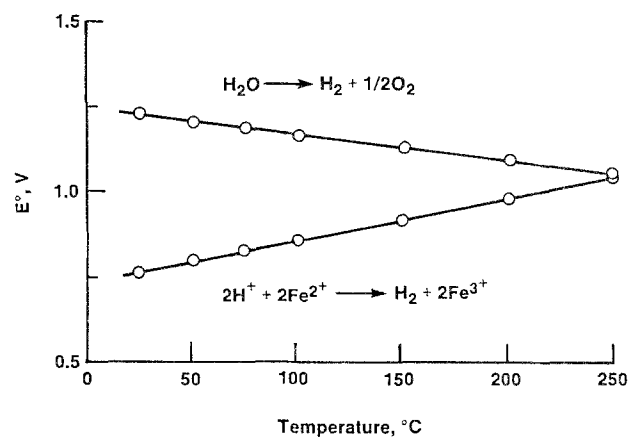


Fig. 12. Thermodynamically calculated electrolysis requirements for water electrolysis and for ferrous to ferric oxidation coupled to hydrogen evolution.

possible that these materials may be suitable as fillers for rubber and plastics in well-defined circumstances.

7. Conclusions

The high-temperature ferric ion oxidation of carbonaceous materials for hydrogen and by-products can be operated as a high-rate, continuous electrochemical process. The economic incentives for operating such an electrochemical process on an industrial scale are at present unclear. However, these may develop with further study of the effectiveness of its unique by-product materials to meet needs in several possible market areas. The extreme low cost of readily available feedstocks such as high-sulphur petroleum coke are a motive to explore the value of possibly up-graded products. Detailed comparisons to mediator regeneration via the air oxidation of ferrous ion (known to be catalyzed by high-surface-area carbon [21]) would be appropriate to compare the economics of the process discussed here with non-electrochemical processes.

Considerations of how much depolarization (vs anodic oxygen evolution) can be achieved in steady-state operation can only be discussed in context of the relative economic values of all products (including the hydrogen) formed. Optimization of temperature, pressure, current density and depth of combustion parameters is similarly impossible in the absence of more information on by-product worth.

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