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Modeling the Anodic Half-Cell of a Low-Temperature Coal Fuel Cell**

*Douglas B. Weibel, Roman Boulatov, Andrew Lee, Rosaria Ferrigno, and George M. Whitesides**

Herein we examine the reduction of Fe^{III} ions by sub-bituminous coal (SBC) having a composition $CH_{0.81}O_{0.22}$ in

[*] Dr. D. B. Weibel,[+] Dr. R. Boulatov,[+] A. Lee, Dr. R. Ferrigno,
    Prof. G. M. Whitesides
    Department of Chemistry and Chemical Biology
    Harvard University
    Cambridge, MA 02138 (USA)
    Fax: (+1) 617-495-9857
    E-mail: gwhitesides@gmwgroup.harvard.edu

[+] These authors contributed equally to the work.

$5 M$ H_2SO_4 at 100°C. The reaction proceeds with a maximum rate constant of 8×10^{-4} $cm\,s^{-1}$,[1] which is 15–160 times greater than those reported previously.[2,3] We used this reaction in the anode compartment of a prototype of a coal fuel cell that operated at 100°C and at atmospheric pressure with VO_2^+ as the model oxidant. The cell produced a maximum current (power) density of 5 A (0.6 W) per liter of a slurry of electrolyte and coal, and 100 mA (11 mW) at the scale at which we carried out experiments (19 mL).

Attempts to develop a process for generating electricity directly from the oxidation of coal date back to the late 19th century.[4] Recent work on coal-powered fuel cells has been motivated by two facts: 1) the worldwide reserves of coal significantly exceed those of other fossil fuels,[5] and 2) the environmental benefits of converting coal into electricity directly in a fuel cell rather than by generating steam in turbines have been perceived as significant.[6] The oxidation of carbon electrochemically has a large activation energy (26 kcal mol^{-1}),[7] and proceeds at room temperature at detectable rates only at an overpotential of greater than 1 V.

Two strategies have been used to overcome the intrinsically slow kinetics of the oxidation of carbon in a coal fuel cell. One strategy is to oxidize a carbonaceous fuel (e.g., graphite) electrochemically at high temperatures (> 600°C)—the majority of recent research on coal fuel cells has been based on this approach.[2,7–9] Molten carbonates are typically used as electrolytes in high-temperature cells; molten hydroxides, borates and silicates, and solid oxides have also been used. One of the most advanced examples of a direct carbon–air fuel cell operated at 630°C for 500 h with molten KOH/NaOH as the electrolyte, a graphite anode that also served as the fuel, and a Fe–Ti alloy as the cathode at which O_2 was reduced. The cell produced current and power densities of 30 A L^{-1} (270 mA cm^{-2} of anode) and 2.5 W L^{-1} (0.12 W cm^{-2} of anode), respectively.[10] The high operating temperature of this class of cells tends to result in their corrosion, particularly in the presence of oxygen.[10] Other technical problems with these cells include: 1) the high resistivity of molten salts (up to 100 Ω cm);[11] 2) the consumption of carbon by reaction with CO_2 to produce CO;[7] and 3) the clogging of cells by ash and other components of the fuel that are not oxidized.[9] The high resistivity and poor mechanical stability of carbon fuels such as bituminous coal make them impractical as consumable anodes in coal fuel cells—the use of coal slurries in molten electrolytes requires vigorous stirring.[6] Zecevic et al. have argued that high-temperature coal fuel cells cannot be made practical because of these problems.[10]

An alternative strategy for overcoming the slow kinetics of the direct electrochemical oxidation of coal is based on the observation that several transition-metal ions, including Fe^{III}, Sn^{IV}, Cu^{II}, and Ce^{IV}, oxidize coal slurries with an activation energy of 7–16 kcal mol^{-1}, which is significantly lower than that for the direct electrooxidation of coal.[12,13] Although the electrolysis of coal slurries in the presence of transition-metal ions has been studied extensively,[2,3,12,13] we are not aware of any coal-powered fuel cells that use a secondary redox couple (e.g., Fe^{III}/Fe^{II}). This type of cell—in which metal ions would be reduced by the coal and reoxidized at the anode electrochemically—has been considered impractical because of the

slow turnover $(< 7 \times 10^{-7} - 2 \times 10^{-5}\,\text{s}^{-1})$ observed under a variety of conditions with all but the strongest oxidants (Ce^{IV} and Br_2).[13]
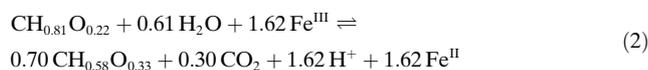
We found that Fe^{II} ions can be generated by reducing a saturated solution of Fe^{III} ions in $5\,\text{M}$ H_2SO_4 (5 mL) with a suspension of SBC (5 g, 70 mesh) at a maximum rate of $4\,\text{mM}\,\text{s}^{-1}$;[14] at this rate and temperature, the reaction becomes kinetically suitable for use in a coal fuel cell operating at atmospheric pressure (although problems with the overall conversion of coal to energy remain; see below).

Among the carbonaceous fuels tested, sub-bituminous coal and Kraft lignin were oxidized most rapidly by Fe^{III} ions.[15] The rates of oxidation by Fe^{III} ions decreased in the order: peat, lignite, activated charcoal, anthracite, and bituminous coal. Graphite felt was inert to oxidation by Fe^{III} ions under these conditions. The oxidation of SBC at $100\,°\text{C}$ by Cu^{II} ions (0.16 V versus the normal hydrogen electrode (NHE)) and Sn^{IV} ions (0.15 V versus NHE)—both weaker oxidants than Fe^{III} ions (0.72 V versus NHE at $100\,°\text{C}$)—was too slow to be useful.[16]

Up to approximately 0.1 mol of Fe^{III} was reduced to Fe^{II} ions with 1 g of SBC (ca. 100 mesh) at $100\,°\text{C}$ in $5\,\text{M}$ H_2SO_4.[15] This amount corresponds to approximately 40 % of the electrons available (0.24 mol or 24 kC) from the complete oxidation of 1 g of SBC to CO_2 and H_2O [Eq. (1)].

$$\text{CH}_{0.81}\text{O}_{0.22} + 1.78\,\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 4.37\,\text{H}^+ + 4.37\,\text{e}^- \tag{1}$$
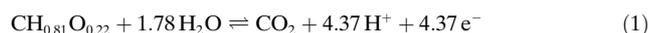
The reaction between SBC and Fe^{III} ions produced CO_2, traces of CO, and a solid with the chemical composition $\text{CH}_{0.58}\text{O}_{0.33}$; the mass of this more highly oxidized residue was 75 % of the initial mass of coal. Equation (2) describes the empirical stoichiometry of the oxidation of SBC by Fe^{III} ions under these conditions.

$$\text{CH}_{0.81}\text{O}_{0.22} + 0.61\,\text{H}_2\text{O} + 1.62\,\text{Fe}^{III} \rightleftharpoons$$
$$0.70\,\text{CH}_{0.58}\text{O}_{0.33} + 0.30\,\text{CO}_2 + 1.62\,\text{H}^+ + 1.62\,\text{Fe}^{II} \tag{2}$$

The rate of reduction of Fe^{III} ions by SBC is given by Equation (3), where $[\text{Fe}^{III}]$ is the concentration of Fe^{III} ions (M); m is the mass of coal (g); l is the average "size" of coal particles based on the mesh size of coal (cm);[17] ρ is the density of coal (g cm^{-3});[18] and v is the volume of the reaction mixture (the volume of the solution and the coal, cm^3). In Equation (3) the term $m/l\rho$ is proportional to the total surface area of the coal; for spherical particles the coefficient of proportionality is 0.75.

$$\frac{\text{d}[\text{Fe}^{II}]}{\text{d}t} = k\,\frac{[\text{Fe}^{III}]\left(\frac{m}{l\rho}\right)}{v} \tag{3}$$

The maximum rate of reduction of Fe^{III} to Fe^{II} ions was $4 \times 10^{-3}\,\text{M}\,\text{s}^{-1}$ at $100\,°\text{C}$ in a reaction mixture containing 5 g of SBC (ca. 70 mesh) and 5 mL of a solution of Fe^{III} ions (0.385 M) in $5\,\text{M}$ H_2SO_4 (this slurry contained approximately 1:1 electrolyte/SBC (v/v)). The corresponding heterogeneous rate constant k [Eq. (3)] was $8 \times 10^{-4}\,\text{cm}\,\text{s}^{-1}$, which is 15–160 times greater than those reported previously for the oxidation of various types of coal by Fe^{III} ions in H_2SO_4 at $100\,°\text{C}$.[2,3]

The kinetic data suggest that the reduction of Fe^{III} ions by SBC under these conditions might provide a method of regenerating Fe^{II} ions in the anodic compartment of a redox fuel cell that uses the $\text{Fe}^{III}/\text{Fe}^{II}$ couple. To explore this possibility, and to identify some of the limitations of such a cell, we built a prototype of a coal fuel cell. In the anodic chamber, Fe^{III} ions were reduced to Fe^{II} ions by SBC, and Fe^{II} ions were oxidized to Fe^{III} ions electrochemically at a carbon felt anode. The anodic oxidation of the Fe^{II} ions was coupled to the reduction of VO_2^+ to VO^{2+} at the cathode (carbon felt) through an external circuit. We separated the cathodic and anodic compartments with a nafion-112 membrane (Figure 1). VO_2^+ is a more suitable oxidant for academic studies than O_2—the species used in commercial fuel cells—because VO_2^+ is a strong oxidant (the standard potential of the $\text{VO}_2^+/\text{VO}^{2+}$ couple is only 0.2 V less oxidizing than that of the $\text{O}_2/\text{H}_2\text{O}$ couple) that is reduced much more rapidly than O_2 at carbon electrodes.

VO^{2+} ions accumulated in the cathodic compartment during the operation of the cell. To regenerate VO_2^+ ions, the solution in the cathodic compartment was pumped into a separate vessel where the VO^{2+} ions were oxidized aerobically in the presence of nitrate at $80\,°\text{C}$.[19]

We ran the cell until the desired fraction of electrons (up to 40 %) available from the complete oxidation of SBC to H_2O and CO_2 had been extracted as electric current. We then separated the remaining solid from the electrolyte by centrifugation, and added a fresh batch of SBC. The content of the cathodic compartment was replaced with a regenerated solution of VO_2^+ ions as frequently as necessary to maintain the cathodic potential within 0.1 V. We observed maximum volumetric current and power densities of 5 A per liter of slurry and 0.6 W per liter of slurry, respectively, using 15 mL of $5\,\text{M}$ H_2SO_4 saturated with $\text{Fe}_2(\text{SO}_4)_3$ and 4 g of SBC (ca. 100 mesh; electrolyte/SBC $\approx$ 4:1 (v/v)). The current/potential curves (Figure 2 a) indicate that the performance of the cell was not limited by the cathodic reaction or by mass transport.

To understand the relative contributions of 1) the reaction between Fe^{III} ions and SBC, 2) anodic oxidation of Fe^{II} ions,
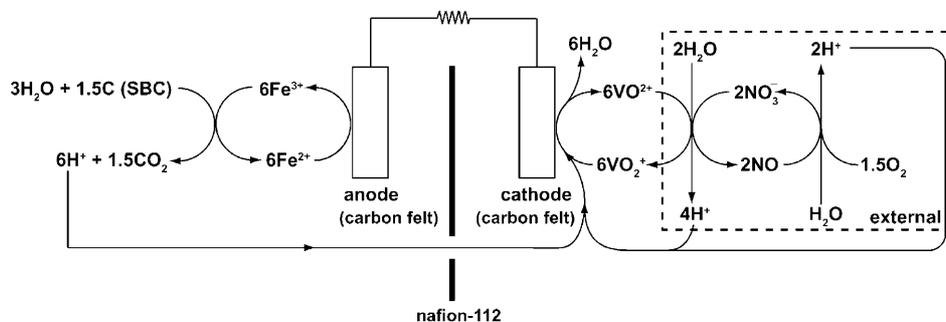

Figure 1. Schematic representation of the coal fuel cell which simplifies the stoichiometry of the reaction between SBC and Fe^{III} ions given in Equation (2).
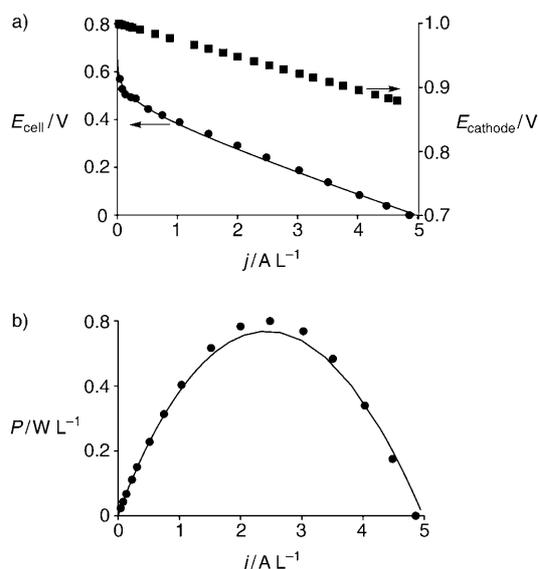
a)

b)

Figure 2. Current and power output of the cell. a) A plot of the potential of the cell E_{cell} (♦, left axis) and the cathodic potential $E_{cathode}$ versus NHE (■, right axis) as a function of the current density j. b) A plot of the power density P as a function of the current density j. The solid lines are fits to Equation (4) using $(km/\rho l) = 0.1$ cm^3 s^{-1}, k_{ET}-$S_{an} = 0.01$ cm^3 s^{-1}, $v = 0.019$ L, $r = 3.90$ Ω. The anodic compartment contained 15 mL of a saturated solution of ferric sulfate in 5 M H$_2$SO$_4$ and 4 g of SBC; the cathodic compartment contained 60 mL of a solution of VO$_2^+$ and VO^{2+} (ca. 1:1) in 5 M H$_2$SO$_4$. The temperature of the cell was 100 °C. The arrows indicate the axes corresponding to each plot.

and 3) cell resistance to the performance of the cell at various currents we analyzed the current/potential and current/power data (Figure 2) with a kinetic model in which Fe^{III} ions were reduced to Fe^{II} ions by SBC with a composite rate constant $km/l\rho$, and Fe^{II} ions were oxidized anodically with a rate constant $k_{ET}S_{an}$; the variables k, m, l, and ρ are defined in Equation (3), k_{ET} is the standard heterogenous rate constant[16] for electron transfer between the Fe$^{III/II}$ couple and carbon felt ($> 1 \times 10^{-5}$ cm s^{-1}, see Supporting Information), and S_{an} is the surface area of the anode (2000 cm^2 for graphite felt with dimensions 13 cm$^2 \times 0.3$ cm).[20] In this model the volumetric current density j [A L^{-1}] is given by Equation (4), where [Fe] is the total concentration of iron (M); v_{an} is the volume of the anolyte (L); E_{cell} is the potential of the cell (V); $E_{cathode}$ is the potential of the cathode (versus NHE, V); $E^{o\prime}$ is the formal potential of the Fe^{III}/Fe^{II} couple under the experimental conditions (0.72 V versus NHE, V); r is the internal resistance of the cell (Ω); F and R are Faraday and gas constants, respectively, and T is absolute temperature (K).

$$ j = \frac{1}{v_{an}} \frac{10^{-3} F \, [\text{Fe}]}{\left(\frac{e^{-\frac{0.5F}{RT}(E_{cathode} - E_{cell} - j\,v_{an}\,r - E^{o\prime})}}{(k_{ET}\,S_{an})} \right) + \left(\frac{1 + e^{-\frac{F}{RT}(E_{cathode} - E_{cell} - j\,v_{an}\,r - E^{o\prime})}}{\left(\frac{km}{l\rho} \right)} \right)} \tag{4} $$

The fit of experimental current/potential curves to Equation (4) (Figure 2) suggests that at potentials below 0.5 V the performance of this prototype fuel cell is limited primarily by the internal resistance (3.9 Ω, a value corre-

sponding to an areal resistance of 50 Ω cm^{-2}). The carbon felt electrodes were responsible for 95 % of this resistance; we estimate the resistance of the nafion membrane and the electrolyte to be less than 0.1 Ω.

At a cell potential between 0.5 and 0.65 V, the rate of the reaction between Fe^{III} ions and SBC limited the current. Our calculations suggest that at the ratio of the area of the anode to the total surface area of SBC used in our experiments $S_{an}/(m/l\rho)$ the electrochemical oxidation of Fe^{II} ions at the anode was not rate-limiting, even at the largest cell potentials.

The open-circuit voltage of our fuel cell was about 350 mV lower than the estimated formal potential of the SBC/O$_2$ couple.[21] The anodic half-cell was responsible for 150 mV of this overpotential, with the steady-state oxidation of Fe^{II} ions by O$_2$, hot H$_2$SO$_4$, or both being probable side reactions.[22] The cathodic half-cell contributed approximately 200 mV to the overpotential, because we regenerated the catholyte only until its potential reached 1 V (versus NHE). The aerobic oxidation of VO^{2+} is relatively slow, and impractically long times were required to achieve [VO$_2^+$]/[VO^{2+}] ≫ 1 that would correspond to more oxidizing potentials. The crossover currents were small (0.5–2 µA cm^{-2} M^{-1}) and contributed little to the overpotential; for example, the loss in a cell comprising two 70-mL compartments separated by a membrane having an area of 13 cm^2 was less than 1 mV per minute when the cell was at open circuit.

As a batch of SBC oxidized, the maximum current density and power produced by the cell decreased as an exponential function of the charge per gram of SBC passed through the cell, because the rate constant for the reaction between Fe^{III} ions and SBC decreased (see Supporting Information).

We ran our prototype fuel cell continuously for 10^3 h (corresponding to the total turnover number of Fe^{III} ions of 10^3) and produced a current that was approximately constant by periodically adding SBC (5 g/100 mL added every 96 h) to the anode compartment and replacing the solution in the cathodic compartment at a frequency that maintained its potential within 0.1 V. The fraction of SBC not oxidized by Fe^{III} ions remained in the anodic compartment during the experiment. We observed no significant degradation in the performance of the cell during this prolonged run.

In summary, we have characterized the kinetics of the oxidation of SBC with Fe^{III} ions at 100 °C and have tested this reaction in a model of the anodic compartment of coal-powered fuel cell. The cell, which contained approximately 4 g of SBC (ca. 100 mesh) and 15 mL of saturated iron sulfate in 5 M H$_2$SO$_4$, delivered a maximum current of 100 mA and a power of 11 mW, which correspond to volumetric densities of 5 A L^{-1} and 0.6 W L^{-1}, respectively. It should be possible to lower the internal resistance of our prototype cell to less than 1 Ω and thereby increase the maximum volumetric current and power densities to over 90 A L^{-1} and 7 W L^{-1}, respectively, simply by optimizing the design of the electrodes, provided that limitations of mass-transport can be avoided. These values compare favorably with the maximum current and power densities reported in the literature for high-temperature coal fuel cells: 30 A L^{-1} and 2.5 W L^{-1}.[23]

The conditions described in the manuscript for the oxidation of SBC do not yet form the basis of a practical

coal fuel cell, because of the small fraction of the enthalpy of SBC that can be converted into electrical power. The reversible electrochemical oxidation of 1 g of SBC with O_2 as the terminal oxidant would produce 24 kC of current at 1 V, which corresponds to 24 kJ of electrical energy. The oxidation of the same amount of SBC by Fe^{III} ions at 100°C in 5 M H_2SO_4 produces 10 kC of current (40%); the remaining 60% of the reducing equivalents are contained in the solid that is oxidized by Fe^{III} ions at a rate below the detection limit of our experiments. At maximal power output, 1.3 kJ of electrical work is extracted from 1 g of SBC (ca. 100 mesh) in our cell; this amount constitutes 5% of the enthalpy of the aerobic oxidation of SBC. Forty-five percent of the remaining enthalpy resides in the unoxidized solid residue. Ohmic resistance dissipates another 5% of the enthalpy (1.3 kJ). The remaining losses (ca. 45%, 11 kJ) arise during the operation of the cell because an equilibrium cannot be maintained between the terminal oxidant (O_2) and the redox couple in the cathodic half-cell (VO_2^+/VO^{2+}) and between the terminal reductant (SBC) and the redox couple in the anodic half-cell (Fe^{III}/Fe^{II}). As a result, the electrolyte in the cathodic compartment is reduced to a greater extent than it would be if it was in equilibrium with O_2, and the anodic compartment is oxidized to a greater extent than it would be if the Fe^{III}/Fe^{II} couple was in equilibrium with SBC. The efficiency of the conversion increases to 7% (2 kJ) if the cell operates at 10% of the maximum power output (high potential); in this regime, the currents are low and the irreversible non-electrochemical oxidation of Fe^{II} ions in side reactions dominates the energy losses. The efficiency of converting the enthalpy into electrical power correlates with the power output only as long as the rate of electrochemical oxidation of Fe^{II} ions exceeds the total rate of non-electrochemical processes in which Fe^{II} ions are oxidized, such as oxidation of Fe^{II} ions by air or H_2SO_4.

The primary reason for the inefficient conversion of enthalpy into power is the exponential decrease in the rate constant with the amount of charge extracted from SBC; this relationship indicates that the rapid initial rate of the reaction between SBC and Fe^{III} ions arises from the oxidation of a small fraction of highly reactive functional groups in coal (probably at or near the surface). As these groups are consumed, less-reactive groups at the surface or in the solid core of the particle are oxidized, with an observed corresponding decrease in the apparent rate constant.

Our analysis of Equation (3) suggests that it should be possible (but untested experimentally) to increase the initial rate of oxidation of coal with Fe^{III} ions by: 1) using smaller particles of coal (decreasing *l*); 2) using a larger ratio of coal to electrolyte (increasing *m/v*); and 3) using a different carbonaceous fuel or different electrolyte (increasing *k*). Improvements (1) and (3) may also increase the number of reducing equivalents of SBC extractable by Fe^{III} ions (namely, >40%). For example, if, following Equation (3), we assume that using particles of SBC with diameters of 1 μm would increase the initial rate of the reaction 200-fold over that with 200-μm particles (100 mesh)—without affecting how rapidly the rate constant *k* decays with the amount of charge extracted per gram of SBC—the enthalpy of conversion would be 9% at maximum power output (17% at 10% of the

maximum power output). If we assume that the rate constant for oxidation of particles of SBC with diameters of 1 μm with Fe^{III} ions decays 200-fold more slowly than for particles with diameters of 200 μm, the efficiency of converting enthalpy into useable electrical energy would become 18% at maximum power output (40% at 10% of the maximum output).[24] By comparison, the corresponding conversion for an internal combustion engine is about 30% and for a proton-exchange membrane (PEM) cell is approximately 45%.[25]

The low efficiency observed in our studies is certainly not inevitable, and can be improved by using a better catalyst for the oxidation of coal than the transition-metal ions screened so far (Fe^{III}, Cu^{II}, Sn^{IV}).

It is possible that the kinetics and extent of oxidation of carbonaceous materials with Fe^{III} ions can be improved by using different fuels. The reactivity of carbon towards the direct electrochemical oxidation in high-temperature coal fuel cells correlates inversely with its degree of crystallinity;[9] a carbon fuel that is more amorphous than SBC may be more reactive to Fe^{III} ions in 5 M H_2SO_4 at 100°C. If the oxidation of coal by Fe^{III} ions requires the coordination of ferric ions to active sites on the surface of coal, H_2SO_4 may not be the optimal electrolyte—Fe^{III} ions are present in H_2SO_4 primarily as $[Fe(HSO_4)_x]^{(3-x)+}$ complexes and the concentration of coordinatively unsaturated ions available for the oxidation of coal is low.[26]

Ultimately, to be practical, the anodic half-cell based on the transition-metal-catalyzed oxidation of a carbonaceous fuel should be integrated with a (half) membrane-electrode assembly (MEA) for the direct reduction of O_2 at the cathode. This integration would be possible only if MEAs are 1) stable to corrosive electrolytes (e.g., 5 M H_2SO_4 at 100°C), and 2) have a low permeability to solutes (e.g., H_2SO_4 and the transition-metal ions).

This study does not provide the basis for a practical low-temperature, coal-powered fuel cell—it demonstrates a significant yield of electrons using what is, in essence, a liquid reformer (the $Fe^{III/II}$ component of this system), and provides a benchmark and starting point against which further studies in this area can be compared.

[1] The units of the rate constant are cm s^{-1}, and arise from the fact that the rate at which Fe^{II} ions are produced is given by d[Fe]/d*t* = *k*[Fe](surface area of coal)/(reaction volume) or [M s^{-1}] = *k*[M][cm^2][cm^{-3}]. These are the same units used for a rate constant for heterogenenous electron transfer between a redox couple in solution and a solid electrode.

[2] P. M. Dhooge, D. E. Stilwell, S.-M. Park, *J. Electrochem. Soc.* **1982**, *129*, 1719–1724.

[3] a) K. E. Anthony, H. G. Linge, *J. Electrochem. Soc.* **1983**, *130*, 2217–2219; b) we estimated a rate constant for the oxidation of lignite coal (mesh >250) at 100°C of 2–3 × 10^{-5} cm s^{-1} by recalculating data from Figure 1 of reference [16] and by using an activation energy of 12 kcal mol^{-1}. We estimated a rate

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constant for the oxidation of bituminous charcoal (ca. 75 mesh) at $100\,^{\circ}C$ of $5 \times 10^{-6}\,cm\,s^{-1}$ by recalculating data from Figure 7 in reference [6] using the reported activation energy of 13.3 kcal mol. The elemental composition of this coal was $CHO_{0.29}$ and the ash content 33%.

[4] See for example: E. Chen in *Fuel Cell Technology Handbook* (Ed.: G. Hoogers), CRC, Boca Raton, FL, **2003**, pp. 2.

[5] a) World Energy Council, "Survey of Energy Resources", can be found under http://www.worldenergy.org/wec-geis/publications/reports/ser/overview.asp, **1998**; b) Energy Information Administration, "International Energy Outlook", can be found under http://www.eia.doe.gov/oiaf/ieo/coal.html, **2004**.

[6] The perceived environmental benefit of converting coal directly into electricity in a fuel cell versus by means of a temperature gradient is the amount of CO_2 released per unit of electrical output. At present, no more than 60% of the enthalpy of the aerobic combustion of carbon can be converted into electricity as a result of the finite top temperature that can be utilized by turbines. A coal fuel cell can convert all of the enthalpy for the aerobic oxidation of coal thermodynamically into CO_2 because of the positive entropy change upon combustion of C to CO_2.

[7] D. G. Vutetakis, D. R. Skidmore, H. J. Byker, *J. Electrochem. Soc.* **1987**, *134*, 3027–3035.

[8] S. Benson, *Fuel Cells: Use with Coal and Other Solid Fuels*, IEA, London, **2001**.

[9] N. J. Cherepy, R. Krueger, K. J. Fiet, A. F. Jankowski, J. F. Cooper, *J. Electrochem. Soc.* **2005**, *152*, A80–A87.

[10] S. Zecevic, E. M. Patton, P. Parhami, *Carbon* **2004**, *42*, 1983–1993.

[11] W. H. A. Peelen, M. Olivry, S. F. Au, J. D. Fehribach, K. J. Hemmes, *J. Appl. Electrochem.* **2000**, *30*, 1389–1395.

[12] A. M. Posner, *Fuel* **1955**, *34*, 330–338.

[13] S.-M. Park, *J. Electrochem. Soc.* **1984**, *131*, 363C–373C.

[14] The composition of SBC after drying was $CH_{0.81}O_{0.22}$; the loss upon drying and ash content were both approximately 10%.

[15] a) This method of burning coal at low temperature reminds us of prior work on oxidatively removing (namely low-temperature burning) lignin from cellulose using polyoxometalates; see, for example: V. Grigoviev, C. L. Hill, I. A. Weinstock in *Fundamentals and Catalysis* (Ed.: D. S. Argyropoulos), American Chemical Society Symposium Series, Washington, DC, **2001**, pp. 297–312; b) lignin, cellulose, and other biomass feedstocks may be particularly attractive fuels in fuel cells because they minimize the emission of CO_2 per unit output of electrical energy.

[16] The standard potential of the $[Fe(H_2O)_6]^{2+}/[Fe(H_2O)_6]^{3+}$ couple is 0.77 V versus NHE: A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, **2001**, 2nd ed. We measured the formal potential in 25% H_2SO_4 at $100\,^{\circ}C$ as 0.57 V versus standard Ag/AgCl, or 0.72 V versus NHE using the potential of the Ag/AgCl reference electrode of 0.15 versus NHE at $100\,^{\circ}C$: D. J. G. Ives, *Reference Electrodes, Theory and Practice*, Academic Press, New York, **1961**, p. 189.

[17] Mesh refers to the number of openings per linear inch of a screen. The mesh size of a particle is the mesh screen having the largest openings on which the particle is retained. The mesh size of the American Sieve Series is related to the size of the opening, in cm as: (size in cm) = 2/(mesh size) for mesh sizes above 50, and (size in cm) = (1.5)/(mesh size) for mesh sizes below 40. In kinetic equations, we used the size of the opening in cm as the characteristic size of a particle of coal l because the linear size is not defined for a particle of an arbitrary shape.

[18] The choice of the parameters $m/l\rho$ to represent the accessible surface is discussed in the Supporting Information.

[19] J. T. Kummer, *Inorg. Chim. Acta* **1983**, *76*, L291–L292.

[20] The measured value for k_{ET} is on the low end of rate constants for electron transfer between the $Fe^{III/II}$ couple and different forms of carbon reported in the literature. See for example, P. Chen, M. A. Frying, R. L. McCreery, *Anal. Chem.* **1995**, *67*, 3115–3122.

[21] We were unable to find data in the literature on the standard redox potential of the reaction in Equation (1) or its temperature dependence. We estimated the potential of this reaction at $100\,^{\circ}C$ from the combustion analysis of SBC, according to the formula: $E_{SBC}(T) = \frac{\Delta G_{combustion}(T)}{nF} - 1.2\,V \approx \frac{LHV}{nF} \approx -0.25\,V$, where the low-heat value (LHV) is the enthalpy of the combustion of coal generating steam and $n = 4.37$.

[22] At open circuit voltage, which corresponds to a potential of the anodic half-cell of about 350 mV versus NHE, the oxidation of Fe^{II} ions by H_2SO_4 becomes thermodynamically favorable at a partial pressure of $SO_2 \leq 600$ Pa ($\leq 0.6\%$ of atmospheric pressure). The aerobic oxidation of Fe^{II} ions is thermodynamically unfavorable at any potential of the cell, but it may be driven by the highly exergonic decomposition of HO_2, which results from reaction between the Fe^{II} ions and O_2. Assuming that the rate of the reduction of the Fe^{III} ions by SBC equals the total rate of oxidation of Fe^{II} ions in side-reactions at open circuit, the apparent first-order rate constant for the non-electrochemical oxidation of Fe^{II} is about $10^{-9}\,s^{-1}$ for a reaction mixture containing 1 g of SBC per 4 mL of 5 M H_2SO_4 saturated with iron sulfate at $100\,^{\circ}C$.

[23] We cannot compare the sustained current and power output of our cell with similar values reported for high-temperature CFCs. The literature on high-temperature CFCs does not specify the fraction of electrons available from the complete oxidation of fuel in the cell that was consumed while the "sustained" performance of the cell was characterized.

[24] The fraction of oxidizable functional groups that are on the surface of a particle of coal is inversely proportional to the radius of the particle when the groups are distributed homogeneously throughout the particle.

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