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Supporting Information

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Oxidation of Coal by Ferric Ion at 100 °C as the Basis for a Coal Fuel Cell

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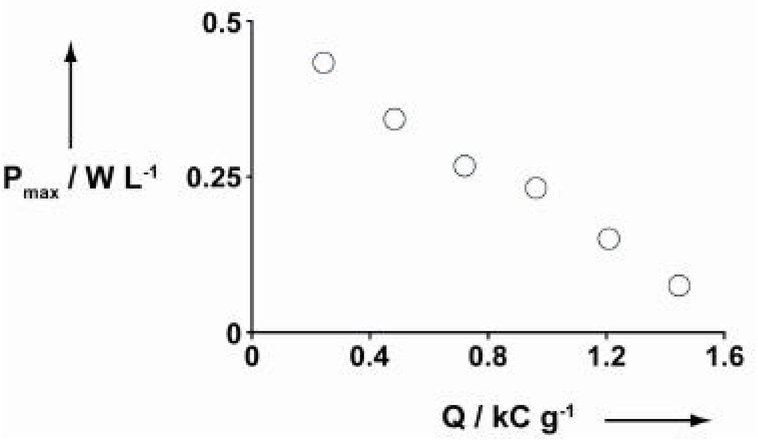

Figure S1: Plot of the maximum power density, P_{max} of the cell as a function of the charge per gram of SBC delivered by the cell, Q. The experimental conditions are the same as in Figure 2 (main text).

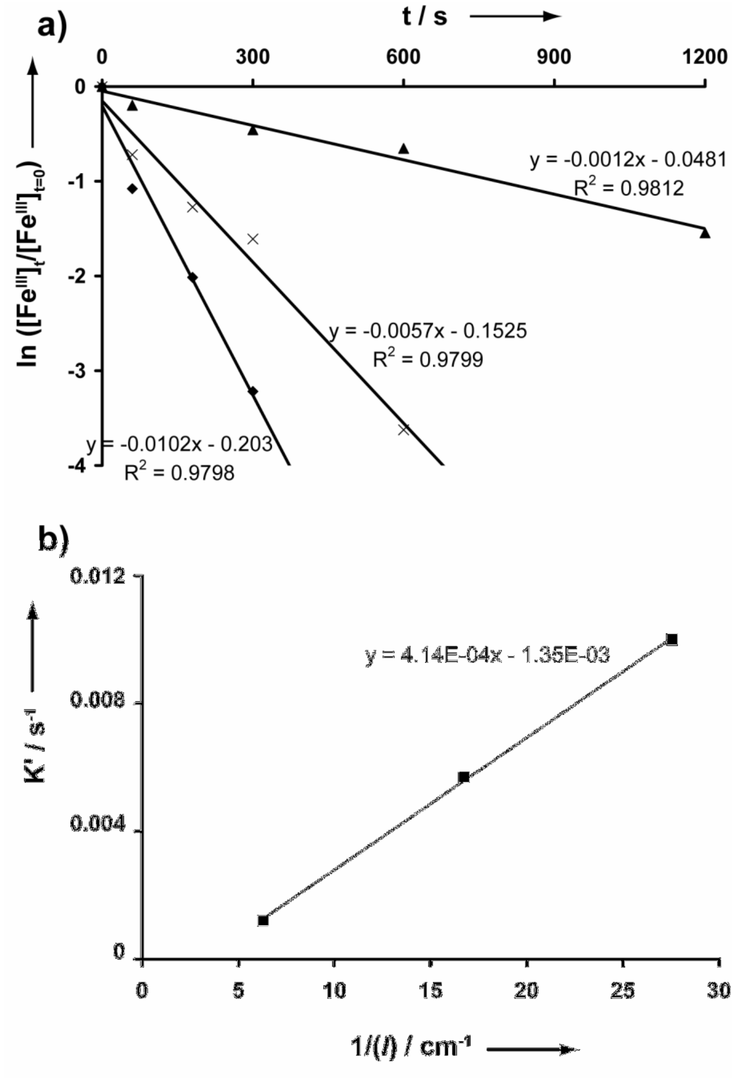

Figure S2: a) A plot of the log of the fraction of ferric ions in the mixture of iron sulfate ($[Fe^{III}]_{t=0}$=0.385 M) and SBC (5 g) in 5 M H_2SO_4, $\log([Fe^{III}]_t/[Fe^{III}]_{t=0})$, as a function of the reaction time, t, at 100 °C for samples of SBC of different particle size. (?) ~ 16 mesh, (×) ~ 40 mesh, (♦) ~ 70 mesh. b) A plot of the pseudo-first order rate constant, k' vs. the average size of coal particles, 1/*l*. Solid lines are least-squares fits to the equations shown.

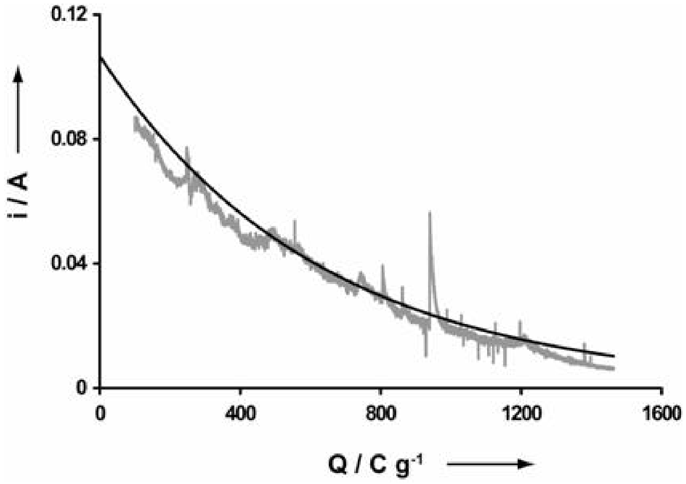

Figure S3: Plot of the current, *i*, obtained by electrolysis of Fe^{III}/SBC mixtures in 5 M H_2SO_4 at 100 °C vs. the charge per gram of SBC, Q, passed through the cell. The black line is the fit to Eq. (S1), where i_0 is the current at Q = 0 C; 10^4 C g^{-1} is the maximum amount of charge that can be extracted per gram of SBC by Fe^{III}; 16 and 9×10^6 are empirical fitting constants and are dimensionless.

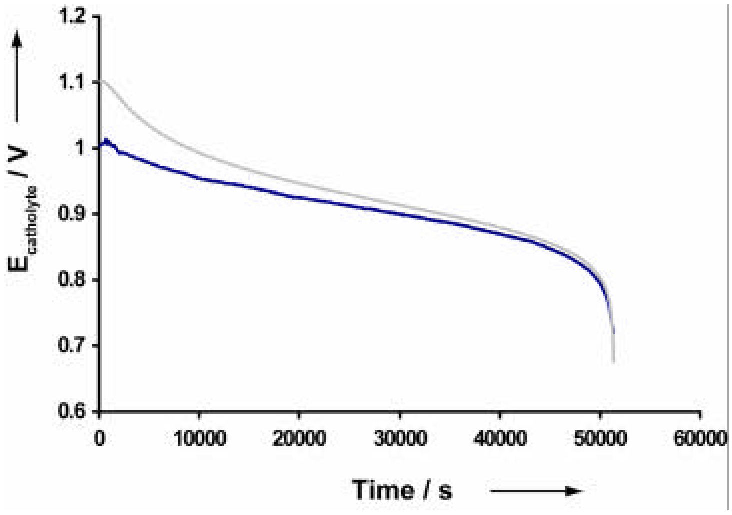

Figure S4: Determination of cross-over currents. The potential of the catholyte (black line) vs. NHE of a cell at open circuit and the data fit to Eq. (S2) (gray line).

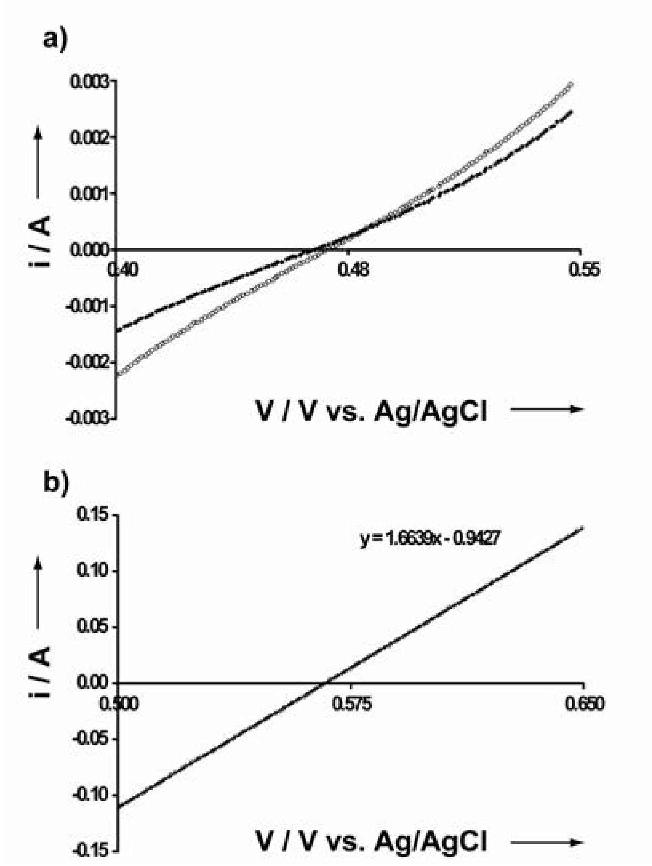

Figure S5: Current-voltage curves measured in 0.5 M $FeSO_4$ and 0.25 M $Fe_2(SO_4)_3$ in 5 M H_2SO_4 using a carbon felt working electrode at a) room temperature (♦ felt used "as received"; o felt after heating in concentrated HNO_3 for 1 hour) and b) at 100 °C. In all cases, the volume of the felt was 0.2 cm^3 and the corresponding surface area was 92 cm^2. Pt wire was used as the auxiliary electrode. In B), the current is limited by the resistance of the cell (0.6 Ω), so that only the lower limit of the rate constant can be determined.

Materials and methods

Experimental Section:

Vanadium ^{IV} sulfate oxide, iron ^{II} chloride, iron ^{III} chloride, iron ^{III} sulfate, tin ^{II} chloride, tin ^{IV} oxide, copper ^{I} chloride, and copper ^{II} chloride, platinum foil (99.9%), and graphite felt (1 cm thick) were purchased from Alfa Aesar. Barium diphenylamine-4-sulfonate, potassium dichromate, and activated charcoal were purchased from Aldrich. Solutions of V^{V} were prepared by electrolyzing a 1M solution of $VOSO_4$ in 5 M H_2SO_4 in a half-cell separated by a Nafion membrane from a half-cell containing 5 M H_2SO_4. Nafion membrane (0.05 mm and 0.09 mm thick) was purchased from Aldrich and activated by heating in 2 M H_2SO_4 at 60 °C for 120 min, then rinsed with deionized water and used immediately. We prepared carbon felt electrodes by boiling the felt in concentrated nitric acid for 15 min. Coal samples were obtained as follows: sub-bituminous (Wyodak Resources, Gillette, WY), bituminous (Williams Coal & Oil, Braintree, MA), anthracite (Williams Coal & Oil, Braintree, MA), lignite (Dakota Westmoreland Corp, Beulah, ND), peat (American Coal Foundation, Washington, DC).

Spectrophotometric determination of the initial rate of oxidation of SBC by Fe^{III}. In a typical experiment, 5 mL of 0.385 M $FeCl_3$ in 5 M H_2SO_4 was heated to 100 °C in a polypropylene tube (50 mL) containing a magnetic stir bar. Coal was added and the reaction stirred (600 RPM) at 100 °C for the allotted amount of time. The solution was immediately cooled in an ice bath, centrifuged for 2 min at 16,000 RPM, and an aliquot removed and titrated with potassium dichromate in the presence of barium diphenylamine-4-sulfonate until a visible end point (purple color) was reached. Experiments were performed in triplicate. This reaction also proceeded rapidly when carried out in 5 M HCl. To measure the rate of Fe^{III} reduction with different ranks of coal, we determined the moisture content of coal samples, and took this into consideration.

Determination of the rate of the reaction between SBC and Fe^{III} as a function of charge extracted from SBC. We carried out the determination of the rate of the reaction between SBC and Fe^{II} as a function of the charge extracted from SBC in a 3-electrode cell at 100 °C. The anolyte consisted of 15 mL of 5 M H_2SO_4 saturated with iron sulfate and 0.3 – 4 g of SBC; the anolyte (5 M H_2SO_4) was separated from the catholyte by a Nafion-112 membrane. The anode (working electrode) was carbon felt and the cathode was platinized titanium. A potential of 1.3 V (vs. NHE) was applied to the working electrode to maximize the steady-state concentration of Fe^{III} and the current was recorded as a function of time (Figure S3). We fit the data to Eq. (S1); the current is 0 when Q = 10 kC g^{-1}.

$$i = i_0 \frac{e^{16\left(1-\frac{Q}{10^4}\right)}-1}{9\times10^6} \qquad \text{(S1)}$$

Oxidation of V^{IV} by NO_3^-/O_2. Vanadium was reformed in a 3-neck round bottom flask (250 mL) equilibrated at 80 °C. The reformer was charged with 150 mL of 1 M VO^{2+} in 5 M H_2SO_4 containing 6% HNO_3 (v/v). After adding 1 g of solid V_2O_5, the reformation reaction was initiated by purging the reactor with O_2. The reformer operated most efficiently under a slight positive pressure of O_2, rather than by passing a stream of O_2 through the chamber, or bubbling the gas through the solution.

Fuel Cell. The fuel cell was composed of a catholyte chamber (70 mL), and an anolyte chamber with a volume of either 20 mL (machined PTFE) or 70 mL (glass) separated by a Nafion membrane (4.3 cm diameter, 0.05 mm thick). Carbon felt (5 cm in diameter, 0.3 cm thick) was used as both the anode and the cathode, and contacted by threading a 4 cm platinum wire (0.5 mm diameter) through each electrode. The separation between the cathode and anode was ~0.6 cm. Carbon felt electrodes were inert to a saturated solution of Fe^{III} in 5 M H_2SO_4 at 100 °C. A solution of Fe^{III} of the desired molarity in 5 M H_2SO_4 was added to the anode half cell and a solution of VO_2^+ and VO^{2+} (total concentration 1 M) in 5 M H_2SO_4 added to the cathode half cell. The cathode half cell was connected to a VO_2^+ reformer via a peristaltic pump that was operated at a flow rate of 200 mL/min.

At the beginning of the experiment, tubing was filled with a solution of VO_2^+ (20 mL total volume). The VO_2^+ reformer consisted of a 250 mL 3-neck round bottom flask equipped with a stir bar and an inlet for O_2. The reformer was initially filled with a solution of VO_2^+ (200 mL). To initiate the reformation reaction, V_2O_5 (1 g) and concentrated HNO_3 (9 mL) were added, and the reformer sealed under an atmosphere of O_2. The temperature of the reformer was monitored using a teflon-coated thermocouple and maintained at 80 °C. To ensure that the relatively slow batch reformation of VO_2^+ would not hamper the performance of the cell, we connected a VO_2^+ reservoir to the fuel cell. The reservoir consisted of a 3-neck 100 mL round bottom flask equilibrated to 80 °C that was filled with freshly reformed VO_2^+ (80 mL). This chamber was connected to both the VO_2^+ reformer and the cathodic compartment of the fuel cell via two peristaltic pumps that were operated at a flow rate of 200 mL/min. After a fresh batch of VO_2^+ had been reformed (~200 min), 80 mL of this solution was pumped into the reservoir. When the catholyte needed to be replaced, we pumped the solution into the reformer; the empty cathode half-cell was refilled with reformed VO_2^+ from the reservoir.

The total volume of VO_2^+ used at the onset of the experiment (fuel cell, reservoir, reformer) was 400 mL. The cathodic half cell was mixed with a magnetic stirrer operating at 600 rpm. We mixed the coal slurry in the anodic half cell with a PTFE stirring shaft (5 mm diameter, turbine-type agitator, Aldrich Z15,470-9) connected to an overhead stirrer operating at 700 rpm. The temperature in the anode half cell was monitored using a PTFE-coated thermocouple, and maintained at 100 ± 1 °C. Once the internal temperature had equilibrated to 100 °C, an aliquot of SBC was added to the anolyte. The current and potential of the fuel cell were monitored using either a potentiostat or a voltmeter (internal resistance, 10 MΩ). The data in Figure S1 were collected by passing a desired amount of charge (calculated from the amount of coal in the anolyte) through the cell at 0 V, refilling the catholyte chamber with freshly-regenerated VO_2^+ solution, and collecting the current/potential curves. The potential of the catholyte was measured with a double-junction Ag/AgCl standard electrode (Omega PHE-3211, operating temperature ≤ 130 °C).

Total turnover number for Fe. The fuel cell was assembled using a Nafion membrane (0.05 mm thick) as described above. Platinum electrodes (2.25 cm^2) were used as both anode and cathode, and contacted with a 4 cm platinum wire (0.5 mm diameter). A 10 mM solution of Fe^{III} in 5 M H_2SO_4 (80 mL) was added to the anode half cell and 80 mL of a 1.0 M solution of VO_2^+ in 5 M H_2SO_4 added to the cathode half cell. The electrodes were connected to an ammeter. The ammeter was in turn connected to a computer that recorded current measurements over time.

Coal was added by removing 10 mL of Fe^{III} solution from the anode half-cell, rapidly mixing it with 10 g of sub-bituminous coal (60-80 mesh), and transferring the resulting slurry to the anode half-cell. The fuel cell was heated to 100 °C. When the current of the cell had decreased significantly due to the consumption of VO_2^+, we pumped out the catholyte and replaced it with a fresh solution. Solutions of VO_2^+/VO^{2+} that were removed from the fuel cell were oxidized electrochemically. In this experiment, we periodically (~ every 4 days) added more coal to the fuel cell to make sure that fuel was present in excess. The total turnover number was calculated by integrating the current over time. This experiment was carried out for one month. Technical issues (e.g. o-rings, leaks, etc.) limited the amount of time this experiment was run.

Determination of cross-over currents. Experiments were carried out in a two-chamber cell at 100 °C; the anodic chamber (70 mL) was filled with 1 M Fe^{II} in 5 M H_2SO_4; the catholyte was 0.15 M VO_2^+ and 0.15 M VO^{2+} in 5 M H_2SO_4. The open circuit potential of the cell, and the potential of the catholyte relative to an Ag/AgCl reference electrode (Omega PHE-3211, operating temperature =130 °C) were monitored over time. Both potentials decreased with time as VO_2^+ was consumed by i) reaction with Fe^{II}, which diffused from the anodic compartment to the cathodic compartment, and ii) the diffusion of VO_2^+ from the cathodic compartment to the anodic compartment. The former process increases the concentration of VO^{2+}. Diffusion of Fe^{III} and VO^{2+} between the two compartments also occurred; the effects of these processes on the potentials were minor and were not considered in our calculations. To determine the average permeation rate, the potential of the cathodic compartment was fit to Eq. (S2) iteratively.

$$E(t) = E_{initial} + 0.031 \times \ln \frac{\left[V^{V}\right]_{initial} - \dfrac{\left(\dfrac{j_{Fe}}{1 + e^{\frac{0.72 - E(t)}{0.031}}} + j_{V^{V}} \right)}{V_{catholyte}}}{\left[V^{IV}\right]_{initial} + \dfrac{j_{Fe}}{V_{catholyte}}} \qquad \text{(S2)}$$

$[V^V]_{initial}$ and $[V^{IV}]_{initial}$ are the initial concentrations of VO_2^+ and VO^{2+} in the cathodic compartment, $V_{catholyte}$ is the volume of the catholyte, j_{Fe} and j_V^V are the fluxes of Fe^{II} and VO_2^+ to and from the cathodic compartment and are given by Eq. (S3) and Eq. (S4).

$$j_{Fe} = j^{o} \left(1 - \frac{1}{V_{anolyte}} \int_0^t j_{Fe}(t)dt \right) \qquad \text{(S3)}$$

$$j_{V^{V}} = j^{o} \left(\left[V^{V}\right]_{initial} - \frac{1}{V_{catholyte}} \int_0^t j_{V^{V}}(t)dt \right) \qquad \text{(S4)}$$

In Eq. (S2) the term $\dfrac{1}{1 + e^{\frac{0.72 - E(t)}{0.031}}}$ quantifies the fraction of Fe^{II} that has diffused from the anodic compartment to the cathodic compartment, and is oxidized by VO_2^+ (0.72 V is the formal potential of the $Fe^{III/II}$ couple and 0.031 V = 1/f at 100 °C). In Eqs. (S3-4) the integral corrects the flux for the depletion of the diffusing species in their reservoir.

An explanation of the use of the parameter m/*l*ρ to represent accessible surface. The surface area of a single particle can be estimated from the mesh size; to know the total surface area of a sample of coal with mass m, we needed to know the total number of particles. The total number of particles is obtained by dividing the total volume of a sample by the volume of a single particle; to determine the total volume of the sample, we needed to know the density. We introduced *l* as a variable (a) to eliminate confusion due to the “unusual” unit of the mesh size, cm^{-1}, and (b) because the size of the opening of a screen with a specific “mesh” size is not simply 2.54/mesh in cm^{-1} (see footnote 17 in the paper). Finally, *l* is not simply a “size” of a particle, because for a particle of an arbitrary shape, linear size is undefined.