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Use of magnetite as anode for electrolysis of water

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We have studied the oxidation of magnetite to Fe$_2$O$_3$ in an electrolytic cell in which the anode is magnetite and the cathode is platinum. We report cyclic voltammogram data consistent with the hypothesis that magnetite, without oxygen gas production but with hydrogen gas production at the cathode, is occurring. The reaction occurs at a potential at the anode of about 0.3 V vs SCE in 1 M NaOH electrolyte, consistent with colloid experiments which also estimated the equilibrium potential of the hypothesized reaction. Electrode characterization results using BET, XEDS, and macroscopic volume and mass measurements are reported, as well as the measurements of the amount of hydrogen gas generated per unit current. The quantity of gas generated is also consistent with our hypothesis concerning the electrode chemistry. Some samples exhibit evidence of two oxidation reactions occurring at the anode and a possible interpretation of these is also discussed. These results suggest the use of magnetite as an anode in a cell electrolysing water to produce hydrogen gas and Fe$_2$O$_3$. In such an electrolyser, the electrical energy cost of producing hydrogen gas could be significantly lower than the cost in a standard electrolyser. The measured steady state currents, equivalent to about 400 mA/g of magnetite, are too low to make a practical electrolyser. We briefly discuss several ways in which the currents might be increased to the levels required. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4730777]

I. INTRODUCTION

The intermittency of renewable energy sources, particularly wind and solar, is a major concern in current planning for reduction of the dependency of the US energy economy on fossil fuels.\(^1\) While “smart grid” technologies will partially alleviate this problem, another component of the solution is likely to be improved energy storage technologies which can act as “capacitors” to store energy until it is needed on the grid. Storage technologies include pumped water in dams, compressed air, flywheels, and hydrogen and other generated fuels. Storage of energy in the form of gaseous hydrogen has been discussed for at least three decades in this application.\(^2\) Solar photovoltaic and wind resources would generate energy in electrical form and the electrical energy not used immediately in the grid would be used to produce hydrogen gas, usually by electrolysis, but also, in the case of solar sources, by direct photoelectrolysis in electrochemical solar cells.\(^3\) The hydrogen generated then needs to be stored, transported and oxidized to regenerate water and useful forms of energy. There are technical issues at each stage of this process, which have been under intensive study.

In this paper, we report results of experiments on a proposed new technology for the first step in this sequence, the generation of hydrogen by electrolysis. Current electrolysis efficiencies are around 66%. The US Department of Energy has articulated a goal of 75% to improve the overall efficiency of the use of hydrogen as a buffer in a renewable energy system.\(^4\) Attempts to improve electrolysis efficiency include studies of proton exchange membrane electrolysis systems in which the emphasis is on improvement in the transport properties of the electrolyte\(^5\) or in catalytic improvement in the rate of the anodic reaction.\(^5\)

Here we study another approach, namely, the use of a consumable anode which provides some of the free energy required for electrolysis, thus reducing the required electrical energy for production of hydrogen. We have found very few references to this approach in the literature. Notably, Ref. 7 reported some success using pyrite as the anode material. That reference reported hydrogen production at the cathode with an anode potential more than half a volt below the anode potential required for oxygen evolution. If comparable steady state currents could be achieved, then that could lead to substantial savings in the electrical energy cost of generating hydrogen. Unfortunately the currents observed were substantially lower than those obtained in an electrolyser with oxygen evolution at the anode. Other work\(^6\) recent work on electrolysis uses consumable carbon anodes, with the generation of carbon dioxide at the anode. The latter method gave large hydrogen yields at low voltages but, as a practical technology, it leaves unsolved the problem of the disposal or sequestration of the resulting carbon dioxide.

Similar but different chemical ideas for the utilization of reactions like the ones using iron oxides which we study here for hydrogen generation have been reported in Ref. 9. The use of taconite as a catalyst for the splitting of water for generation of hydrogen has been mentioned several times in the literature and is the subject of at least one patent.\(^10\) However that work reported the use of heat, rather than electrical energy, to drive the electrolysis reactions.

We study the possibility of oxidizing magnetite by the oxygen in water with the production of Fe$_2$O$_3$ and hydrogen. The process is endothermic and we explore the feasibility of supplying the required additional energy electrochemically. We studied the reaction (in acid media),
A byproduct is Fe$_2$O$_3$, probably in the form of maghemite (γ-Fe$_2$O$_3$). It might be possible to store the hydrogen on site and then, when electricity demand is high or renewable wind or solar energy is not available, to run the same device “backward” as a fuel cell, thus recovering both the energy stored in the hydrogen and the energy stored in the Fe$_2$O$_3$ or other oxidised product. Alternatively, the Fe$_2$O$_3$ might be removed and replaced by unoxidised magnetite in the electrolyser. The Fe$_2$O$_3$ might then be used, discarded, or regenerated by other chemical processing. We do not report any experimental studies of any of these options in this paper. It should be noted, however, that any of them will entail costs which will have to be considered in evaluating the net efficiency gain if such a process were to be implemented in an electrical generating system.

The magnetite reaction at the anode has been studied in a colloid science context and the equilibrium potential as a function of pH was reported. For quantitative theoretical analysis, using information about the redox potential of the reactions as a function of the pH of the electrolyte available in the literature we can determine the expected equilibrium potential and we attempted to make calculations predicting the expected rate of hydrogen production in the cell. Information is available concerning electrical resistivity of magnetite and hematite (which appear adequate) and the rate of oxygen diffusion ($<10^{-18}$ cm$^2$/s) at room temperatures. Using a simple analysis described in Appendix A, we got estimates of the expected dc currents from samples with reactive areas similar to those of the samples studied in the work reported here and for possible ranges of the unknown parameters $v_0$ and $D_{Fe}$ as shown in Fig. 1. The very wide range of possible currents indicated that experiments were required to get a more quantitative understanding.

II. MAGNETITE ELECTRODE PREPARATION AND CHARACTERIZATION

Magnetite was acquired in the form of magnetic “sand.” In order to make pressed magnetite samples for use as electrodes, we constructed a die set that was designed to be operated in a 20 ton hydraulic press. The die set was
constructed to produce cylindrical samples (approximately approximately 1/8" in diameter by 1/4" long) which fit into the electrochemical apparatus. The resulting magnetite samples were affixed to clean copper wires using silver solder (Electrodag 5810). The lead ends of the electrodes were dipped into plastic dip to cover the silver solder and copper wire and allowed to dry. The last step assured that the silver solder and copper wire did not interact with the electrolyte during the experiment. Fig. 3 shows a photograph of an electrode and the results of energy dispersive x-ray analysis (XEDS) of the chemical content of one of them. Quantitative results of the x-ray analysis appear in Table I.

An electron micrograph of the surface of a portion of one of the electrodes with resolution in the submicron range is shown in Fig. 4. To get further information on the morphology, we obtained Brunauer-Emmett-Teller (BET) measurements\textsuperscript{15} of some of the electrodes. By measuring the volumes of two of the electrodes for which BET measurements were made, we found the results shown in Table II. The first sample was made using magnetite powder as purchased and the second was made with powder which had been crushed in our laboratory. The surface areas measured by the BET method were both smaller than those found with the Langmuir method but all were in the range 0.3 to 0.8 m\textsuperscript{2}/g. The additional crushing which we did increased the area only modestly, by about a factor of 2 or less. We get a nominal particle size $l$ from the reciprocal of the area per gram times magnetite density, giving values from 0.24 to 0.73 $\mu$m. By determining the mass $M$ and volume $V$ of the samples, we obtain an estimate $M/V$, also listed in Table II, of the volume fraction of the samples which are magnetite. These filling fractions are close to 0.5. These numbers are consistent in order of magnitude with those inferred from visual inspection of the micrograph in Fig. 4.

### III. ELECTROCHEMICAL MEASUREMENTS

One of the electrochemical cells used for the experiments is shown in Fig. 5. In Fig. 6, we show cyclic voltammogram (CV) data from one of the (uncrushed) magnetite electrodes in 1 M NaOH (pH 14) solution together with a simulation of the CV. (Experiments using perchloric acid electrolyte with pH in the range of 2 to 3 showed strong indications of iron dissolution from the sample into solution and were not pursued further.) At these high pH levels, the

<table>
<thead>
<tr>
<th>Element</th>
<th>wt. %</th>
<th>at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>2.07</td>
<td>5.33</td>
</tr>
<tr>
<td>O</td>
<td>27.68</td>
<td>53.61</td>
</tr>
<tr>
<td>Na</td>
<td>0.53</td>
<td>0.72</td>
</tr>
<tr>
<td>Mg</td>
<td>0.28</td>
<td>0.36</td>
</tr>
<tr>
<td>Al</td>
<td>0.63</td>
<td>0.72</td>
</tr>
<tr>
<td>Si</td>
<td>1.45</td>
<td>1.60</td>
</tr>
<tr>
<td>Ti</td>
<td>2.91</td>
<td>1.88</td>
</tr>
<tr>
<td>Fe</td>
<td>64.45</td>
<td>35.77</td>
</tr>
</tbody>
</table>
current is expected to be carried by hydroxyl ions in the electrolyte, so that the reactions occurring at the electrodes at the peak in the anodic sweep become, according to our hypothesis
\[
2Fe_3O_4 + 2OH^- \rightarrow 3Fe_2O_3 + 2e^- + H_2O
\]
at the magnetite electrode and
\[
2H_2O + 2e^- \rightarrow 2OH^- + H_2
\]
at the platinum counter electrode. Some details of the simulation methods appear below and in Appendix B.

There is a clear signature in Fig. 6 near the anticipated potential, suggesting that we are in fact observing the hypothesized reaction. We have observed this peak at a series of pH values (all in NaOH) and compare the observed peak positions with the values reported in Ref. 11 as shown in Fig. 7. (We think it likely that the reaction (3), not Eq. (1), also was occurring in the high pH colloid experiments reported in Ref. 11.)

The modelling of the cyclic voltammetry data on magnetite electrodes was carried out with a Fortran code written by us following the general approach described in Ref. 16 and reviewed in Appendix B. We wrote a Monte Carlo search routine to optimize the fit of the resulting CV characteristics to the experimental one, allowing the values of the parameters $R$ (solution resistance) $k_{app}$, the rate constant, $A$ the effective surface area and the diffusion constants $D_{ox}$ (taken to be the diffusion constant of Fe$^{2+}$ in the magnetite electrode) and $D_{red}$ (taken to be the diffusion constant of the ferric ions in Fe$_2$O$_3$) to vary. The equations are solved to express the surface current (at $x = 0$) in terms of the densities at $x = \Delta x$ as in Ref. 16.

In Fig. 6, the fit to the model is moderately good. The area parameter found from the fit (508 cm$^2$) is larger than the BET area (see Table I: the area is 0.2650 m$^2$ measured in a different, but similar electrode, but of the same order of magnitude. The fit value for the diffusion constant of the ferrous ion ($D_{Fe^{2+}} = 9.52 \times 10^{-17}$ cm$^2$/s) is in the range of estimates we find in the literature: For example, in Ref. 17 measurements at 550 °C are reported. In that report, vacancy and interstitial diffusion mechanisms are discussed and the rate is reported to be very sensitive to the molecular oxygen density gradient across a magnetite layer. The sign of the temperature dependence changes as the magnitude of this oxygen activity gradient is varied and becomes negative (increasing diffusion rate with decreasing temperature) at the higher oxygen activities. Diffusion constants in the range $10^{-14}$ to $10^{-16}$ cm$^2$/s were reported. We have been unable to find many reported measurements of ferrous iron diffusion rates in γ-Fe$_2$O$_3$ (sometimes called maghemite) which is likely$^{18}$ to form on the surface of magnetite as water splitting proceeds at the surface. There is a report in Ref. 19 in which estimates between $1.3 \times 10^{-17}$ and $5.746 \times 10^{-18}$ cm$^2$/s at 200 °C are given. The value of the diffusion constant of the oxidized species, termed “Fe$^{3+}$” in Appendix B is $5 \times 10^{-13}$ cm$^2$/s in the fit. This is also in the range of expected solid state diffusion rates. The fit diffusion constant is 8 orders of magnitude smaller than the diffusion constant of a hydroxyl ion in our electrolyte, so solid state diffusion is limiting the reaction rate.

The fit value of the capacitance (8.43 $\times 10^{-7}$ F/dm$^2$) obtained from the fit is about an order of magnitude smaller than expected for an electrolyte at this molarity. The large listed value of $k_{app}$ is not significant because the simulations showed that the results were very insensitive to $k_{app}$, indicating that the current is diffusion limited, as expected in view of the small values of the diffusion constants.

To check that the reactions associated with the CV peaks were occurring on the magnetite, we carried out a null
experiment in which the magnetite electrode was replaced by a platinum electrode under the same conditions with results shown in Fig. 8. It is clear that no anodic currents occur in the regions of the oxidation and reduction peaks observed with the magnetite anode.

We carried out a dc experiment by stopping the CV sweep at various potentials near the positive peak. Characteristic data on the resulting current as a function of time is shown in Fig. 9. The observed time dependence is fit quite well with two exponential decays and a constant asymptotic current, as shown. The fit suggests a dc current of about 32 μA for this electrode at this potential. Assuming that the particle sizes are of order 0.5 μm (Table II) and a value of $9 \times 10^{-17}$ cm$^2$/s (from the CV fit) for the rate limiting diffusion constant, and assuming that the charge carriers in the electrode consist of one ferrous iron per formula unit, we can estimate the expected dc current, assuming a total sample surface area of about 300 cm$^2$ (between our BET measurement and the CV fit value). We get an estimated current of somewhat less than 1 μA, which is about an order of magnitude less than the estimated asymptotic current from the direct dc measurement.

Such asymptotic currents were determined for several electrodes, giving values in rather wide range from 1 to 100 μA. With surface areas between 100 and 500 cm$^2$, this corresponds to currents in a range between $2 \times 10^{-8}$ and $10^{-6}$ A/cm$^2$. The rather wide range of current values suggests a need for better control of sample quality, but is partly due to different effective surface areas, which could not be measured in every case. As we have not yet carried out reverse operation (corresponding to running the cell as a fuel cell), we could not restore each electrode after each stopping potential run and could therefore not determine whether the asymptotic current as a function of stopping potential behaved as expected from the Butler Volmer relation.
To confirm that the expected amount of hydrogen gas is generated at the Pt electrode during some of these dc experiments, we measured the volume of gas emitted and the current passed. We confirmed that the amount of gas produced was quantitatively that expected (within experimental uncertainties) from the integrated current. For example, in one such experiment we collected $1.4 \times 10^{-5}$ l of gas under standard conditions (approximately 300 K, 1 atm) giving $3.4 \times 10^{18}$ molecules, while the average current was $2.83 \times 10^{-3}$ A for 1470 s corresponding to $1.3 \times 10^{19}$ molecules. The discrepancy of a little more than a factor of three may be attributable to losses in the gas collection system and the approximate values of room pressure and temperature, which were not measured. We also confirmed by mass spectroscopy that hydrogen was present in the gas produced, but the instrument available was not configured to produce a quantitative estimate of the amount.

The cyclic voltammograms obtained from some samples were more complicated than the one shown in Fig. 6, with two or even three peaks during the cathodic sweep within the same potential range indicated in Fig. 6. An example of such data is shown in Fig. 10. Hydrogen was also produced from such electrodes. Dispersive x-ray analysis indicated that when such samples were polarized for a long time at voltages in the region of the peaks the iron/oxygen ratios in the anode were close to 2/3 indicating that these anodes were nearly fully oxidized to Fe$_2$O$_3$. One the other hand, similar x-ray analysis of anodes exhibiting just one peak in the cyclic voltammograms as in Fig. 6 often exhibited iron oxygen ratios closer to 1/2. One possible interpretation of these results is that the reaction proceeds in two steps,

$$Fe_3O_4 + OH^- \rightarrow 3FeOOH + H_2O + e^-,$$

followed by

FIG. 8. Cyclic voltammogram data under the same conditions with a platinum working electrode.

FIG. 9. Current after stopping the potential sweep at 0.673 V SCE on the positive sweep with fit to two exponential decays and a constant steady state current. For this sample, the current decay was well characterized by two exponential decay terms with time constants of 62.5 s and 500 s and an apparent asymptotic dc current of 32 µA.
\[ \text{FeOOH} + \text{Fe}_3\text{O}_4 + \text{OH}^- \rightarrow 2\text{Fe}_2\text{O}_3 + \text{H}_2\text{O} + e^- \]  (7)

In such an interpretation, only the first reaction would be going to completion in the samples showing one peak in the voltammograms, whereas both reactions would be completing in the samples showing two peaks in the voltammograms. This hypothesis seems consistent with the limited data which we have but cannot be regarded as having been definitively established by this work. In particular, the occasional presence of a third peak is not explained.

IV. DISCUSSION

The results show that the proposed reactions can be induced electrochemically in the proposed manner to yield hydrogen gas. Priorities for further scientific investigation include improved sample reproducibility, quantitative mass spectroscopic analysis of the gas produced and further x-ray dispersive study of electrodes showing one and two peaks to test the hypothesis that there is an intermediate reaction yielding ferrioxyhydroxide. The hypothesis suggests that the “one peak” electrodes after dc polarization should contain hydrogen which may be detectable by NMR or x-ray dispersive analysis, whereas “two peak” electrodes should not.

For practical purposes, though the samples exhibited a rather wide range of currents, the average current attained so far is too small for the proposed application. Estimates based on the currents observed in the work reported here indicate that many metric tons of magnetite would be required in the electrode of an electrolyser for a 1 MW wind generating station. Clearly, this is impractical and a way must be found to increase the current.

We are exploring several possible ways to increase the current including decrease of particle size, the use of different materials and increase of the operating temperature. Estimates based on the currents observed in the work reported here indicate that many metric tons of magnetite would be required in the electrode of an electrolyser for a 1 MW wind generating station. Clearly, this is impractical and a way must be found to increase the current.

We are exploring several possible ways to increase the current including decrease of particle size, the use of different materials and increase of the operating temperature. The effective reacting surface area may be increased by fabricating the electrodes in a carbon medium, as is done for preparation of fuel cell electrodes. In principle, one could decrease the magnetite particle size to a few nanometers (though scaling this to large systems might be prohibitively expensive). We expect that the current should increase roughly as the inverse square of the particle size: For fixed macroscopic volume, the surface area will increase inversely with the particle size and the diffusive density gradients within the particles will also scale as one over the particle size. Thus going to nanoparticle sizes could increase the current by as much as a factor of $10^6$ which would very substantially reduce the required electrode mass for a wind generator.

Another direction of investigation is the use of related but different materials. A perusal of the Fe-O-S phase diagram in Ref. 21 suggests minerals such as pyrite and pyrrhotite (FeS$_{1-x}$) which are naturally abundant and contain substantially more ferrous iron than magnetite. We will investigate them to determine if they produce higher currents in a similar scheme.

A third option for increasing the current is to increase the operating temperature, which will increase the solid state diffusion and reaction rates. Working in a pressurized vessel, the temperatures could be substantially increased.

For practical application it would be very desirable to make a hydrogen generator of this type reversible, so that by bubbling hydrogen past the platinum electrode one could reverse the reactions, regenerate the magnetite (or other material containing reduced iron) and harvest the electrical energy from the hydrogen. We point out that, if other aspects could be resolved, the capability to run the cell in reverse as a fuel cell in this way is not an absolute requirement: Conceivably, the hydrogen could be used in another fuel cell or used in internal combustion engines and the oxidized product could be removed and discarded or sold if it were marketable.$^{22,23}$

To lower costs, it would be desirable to avoid the use of platinum in the cathode of an electrolyser and we have found in preliminary experiments that copper works quite well. Another option for the cathode, recommended for use in such applications in strong base, is Raney nickel.$^{24,25}$  

![](image) FIG. 10. Cyclic voltammagram from a magnetite anode showing two peaks.
will explore the use of these less expensive metals in future work.

ACKNOWLEDGMENTS

This work was supported by a grant from the Center for Urban and Regional Affairs at the University of Minnesota and by the University of Minnesota Supercomputing Institute. We are extremely grateful to Professor William Smyrl for allowing the use of his laboratory for this investigation and for frequent advice and counsel. We are grateful for the assistance of Research Experiences for Teachers interns Eric Kelhoe and Jeremy Kersten and undergraduate assistants Noah Trebesch and Heather Blundell in this work.

APPENDIX A: PRELIMINARY CURRENT ESTIMATES

In a steady state, diffusion will result in an approximately linear profile of the reactant, Fe^{2+}, across a region in the magnetite electrode of the order \( L \) of its size which we take to be about \( 10^{-3} \) cm. If the positive axis is in the direction from the interface into the magnetite electrode then the current density (which will be negative when the forward reaction dominates) will be

\[
j_{Fe^{2+}} = (DF_{Fe^{2+}}/L)(n_{Fe^{2+}}(0) - n_{Fe^{2+}}(L))
\]

where \( k_b \) and \( k_f \) are forward and backward rate constants.

The equation is easily solved for \( n_{Fe^{2+}}(0) \), the volume density of ferrous ion at the surface of the electrode, in terms of the other variables and reinserted in the expression for \( j_{Fe^{2+}} \) giving

\[
j_{Fe^{2+}} = \frac{DF_{Fe^{2+}}/L}{D_{Fe^{2+}}/L + k_f} (-k_f n_{Fe^{2+}}(L) + k_b n_{Fe^{2+}}(0)).
\]

We take \( n_{Fe^{2+}}(0) \approx 2n_{Fe^{2+}}(L) \) assuming that ferric ions are not significantly depleted at the surface.

APPENDIX B: CV SIMULATION

We suppose that the availability of OH\(^-\) or H\(^+\) is not rate limiting and simplify the reaction to

\[
Fe^{3+} + e^- \rightarrow Fe^{2+},
\]

anticipating that solid state diffusion of the iron species or the rate of the reaction at the surface will be the slowest processes. Then the currents of the reactants are described by the equations given by Orlik.\(^{16}\) Diffusion equations for the ferrous and ferric ions in the magnetite describe the transport

\[
\frac{\partial c_{Fe^{2+}}}{\partial t} = D_{Fe^{2+}} \left( \frac{\partial^2 c_{Fe^{2+}}}{\partial x^2} \right),
\]

\[
\frac{\partial c_{Fe^{2+}}}{\partial t} = D_{Fe^{2+}} \left( \frac{\partial^2 c_{Fe^{2+}}}{\partial x^2} \right),
\]

and boundary on the current at the surface

\[
j_{Fe^{2+}}(x = 0, t) = -j_{Fe^{2+}}(x = 0, t) = -(k_f c_{Fe^{2+}} - k_b c_{Fe^{2+}}),
\]

with the rate constants given by the Butler-Volmer relations\(^{26}\)

\[
k_f = k_{app} \exp(-\alpha |e|(V_{eff} - V_0)/k_B T), \tag{B5}
\]

\[
k_b = k_{app} \exp(\beta |e|(V_{eff} - V_0)/k_B T). \tag{B6}
\]

In the simulations, we took \( \alpha = 1/2 \) so that \( \beta = 1/2 \). We use a “physicist’s” notation in which potentials are represented by subscripted symbols \( V \), the Faraday constant \( F = |e|/N_{au} \), the gas constant \( R = N_m k_B \), Avogadro’s number is \( N_{au} \), Boltzmann’s constant is \( k_B \), and magnitude of the electronic charge is \( |e| \). \( V_{eff} \) takes account of the ohmic resistance \( R \) of the solution and the capacitance \( C \) (per unit of electrode surface area \( A \))

\[
V_{eff} = V_{ext}(t) - (I_F + I_c)R. \tag{B7}
\]

Here \( I_F = j_{Fe^{2+}}A \) where \( A \) is the area of the electrode.

We simplified the electrodynamics of Orlik’s model by taking

\[
V_{ext} = v_{sweep} t \tag{B8}
\]

and

\[
I_c = CA v_{sweep}. \tag{B9}
\]

This causes the observed current to jump when the sweep rate \( v_{sweep} \) changes sign as one can see happening in the simulated cyclic voltammagrams. It implicitly assumes that the \( RC \) time constant of the solution is much smaller than the time scales of interest. The results indicate that this is a reasonable, but not precisely accurate, assumption.

The numerical implementation was very similar to the one described by Orlik. To fit the resulting voltammograms to the experimental data we wrote a Monte Carlo code which searched the 6 dimensional parameter space of the quantities \( (R, k_{eff}, A, D_{Fe^{2+}}, D_{Fe^{2+}}, C) \). The quality of the fits to the cyclic voltammograms exhibiting one peak in the cathodic sweep is moderately good as illustrated in Fig. 6. Most of the parameters determined from the Monte Carlo fit are comparable in order of magnitude or better with our other measurements (such as sample surface area) and with values found in the literature as discussed in the text. The fit is not sensitive to the value of \( k_{eff} \) suggesting that the reaction is primarily diffusion limited as anticipated. To achieve the one peak condition, we constrain the sweep to stop well below the oxygen reduction peak. A model for the two peak voltammograms for which we proposed a chemical model in the text (Eqs. (6) and (7)) was not produced.


Acquired from http://www.magneticsand.com and from Sigma Aldrich, Case No. 1317-61-9, Part No. 637106-25g.


