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Dr. 1282

ERDA/NASA/5022/77/2
NASA TM 73716

ELECTROCHEMICAL BEHAVIOR OF 0.2 TO 3 MOLAR FERROUS CHLORIDE - FERRIC CHLORIDE MIXTURES ON EDGE-ON PYROLYTIC GRAPHITE ROTATED DISK ELECTRODES

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July 1977

Prepared for
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Director for Conservation
Division of Conservation Research and Technology
Under Interagency Agreement E(49-28)-1022

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1 Report No NASA TM 73716	2 Government Accession No	3 Recipient's Catalog No

4 Title and Subtitle
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5 Report Date
July 1977

6 Performing Organization Code

7 Author(s)
Riley O. Miller

8 Performing Organization Report No
E-9199

10 Work Unit No

9 Performing Organization Name and Address
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

11 Contract or Grant No

13 Type of Report and Period Covered
Technical Memorandum

12 Sponsoring Agency Name and Address
Energy Research and Development Administration
Division of Conservation Research and Development
Washington, D.C. 20545

14 Sponsoring Agency Code
ERDA/NASA 5022/77/2

15 Supplementary Notes
This report was prepared under Interagency Agreement E(49-28)-1022.

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17 Key Words (Suggested by Author(s))		18 Distribution Statement
Electrochemistry	Carbon electrode	Unclassified - unlimited
FeII - FeIII - Cl^- system	Polarization	STAR Category 23
Redox kinetics	Rest potential	ERDA Category UC-94C

19 Security Classif (of this report)	20 Security Classif (of this page)	21 No of Pages	22 Price*
Unclassified	Unclassified		

* For sale by the National Technical Information Service Springfield Virginia 22161

E-9199

ELECTROCHEMICAL BEHAVIOR OF 0.2 TO 3 MOLAR FERROUS CHLORIDE - FERRIC CHLORIDE MIXTURES ON EDGE-ON PYROLYTIC GRAPHITE ROTATED DISK ELECTRODES

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SUMMARY

Potentiostatic determinations in various mixtures of ferrous chloride ($FeCl_2$) and ferric chloride ($FeCl_3$) with excess hydrochloric acid show rest potentials that are 0.1 volt less electropositive than the theoretical values from the formulated ratios of FeII to FeIII (probably as a result of complexing). The standard rate constant k_s ranges between 1×10^{-4} and 6×10^{-4} centimeter per second. Tafel slopes b of roughly 0.12 volt per decade indicate single-electron exchange kinetics. No significant trend in either b or k_s was attributed to mixture composition. The higher k_s values occurred with an edge-on pyrolytic graphite that had undergone a permanent surface change.

INTRODUCTION

The electrochemical behavior of the redox couple ferrous chloride - ferric chloride ($FeCl_2$-$FeCl_3$) at 0.2 to 3 molar total concentration was explored for two reasons. The first was a practical one; there is the possibility of using highly concentrated acidic solutions of $FeCl_2$-$FeCl_3$ as one of the redox couples in a scheme to store electric energy cheaply for matching power production with demand (ref. 1). This scheme requires efficient, deep, and repetitive oxidation and reduction of high-concentration aqueous electrolytes. It is desirable to know the relative importance of electrochemical reactions in such processes.

Aside from the practical need, a second motive was a concern that electrochemical science now needs to explore redox reactions in aqueous solutions with concentrations higher than 0.1 molar. In this we have made a start.

Potentiostatic polarization data were obtained for two rotated disk electrodes of polished edge-on pyrolytic graphite. Corrections had to be made for current-resistance (I·R) drop. The electrodes were characterized by voltammograms as well as microscopic examination. Our data are compared with those of other investigators. Finally the data are discussed in terms of practical use as well as basic concept.

PROCEDURE

The electrode processes that we are concerned with are steady-state ones, and therefore we wished to obtain data at well-established steady-state conditions. Consequently, transitive techniques were used only to obtain supplemental data, such as I·R drop.

In a steady-state half-cell, if convection is constantly controlled (such as by stirring or by moving the electrode) and if the reaction kinetics does not change with overpotential η, an easy way to determine electrochemically limited current I_c is to increase η to where current is constant and therefore transport limited. This transport-limited current I_T is used to calculate I_c at several lower η by the relation $I_c = I_x(1 - I_x/I_T)^{-1}$, where I_x is measured at η. Unfortunately this method is limited to lower measured currents I_x because of high I·R drop at the higher I_T values.

If a rotated disk electrode (RDE) technique is used, convection is well characterized as a function of rotational speed ω, I_T need not be measured, and higher I_x can be evaluated. At a given η, $(I_c)^{-1} = (I_x)^{-1} - c\omega^{-1/2}$, so that I_c can be calculated if I_x is determined at several values of ω. We elected to use this approach. (These particular aspects are discussed also in ref. 2, pp. 27 to 30; the general methodology of the RDE is reviewed in ref. 3.)

At the high current densities that are expected in this work, the current density at a disk-shaped electrode is not uniform. Nevertheless, we decided that the ease of polishing and an abundant prior art outweighed this disadvantage of the RDE. The maximum edge current density can be estimated from the mean current density by use of Newman's J correction (ref. 4). Our reference well, containing a standard calomel electrode (SCE), was located far from the disk (approximately 2 cm as contrasted to a Luggin capillary about 1 mm from the disk).

Edge-on pyrolytic graphite (EOPG) was chosen as the current collector because it is a fairly well characterized, electrically conductive, electrochemically active, high-density form of carbon, an element that is abundant and corrosion resistant. The RDE, made of this material mounted in fluorocarbon polymer, was hand polished to a mirror finish with moistened 0.1-micrometer diamond dust on a satin cloth. The frontal area of the disk was 0.32 square centimeter. The RDE drive, as well as the electrodes, was fabricated from designs developed at Case Western Reserve University.

The cell, made of borosilicate glass, was cylindrical (6.4 cm in diam, 8 cm high). The counter electrode was carbon cloth supported at the inside perimeter of the cell by a poly-fluorocarbon mesh form. It was approximately 6 centimeters in diameter and 5 centimeters high (the depth of the electrolyte in the cell). The real surface area of the counter electrode was over 200 square centimeters. The reference electrode well was a sidearm connected to the cell by a tube which flared into the bottom center of the cell about 2 centimeters from the RDE. This tube contained a finely sintered glass plug to slow diffusion of FeII into the well, which contained 1 molar hydrochloric acid (HCl). A snugly fitting polypropylene lid isolated the cell from the atmosphere.

The electrolytes were solutions of $FeCl_2$, $FeCl_3$, and HCl in distilled water. In most of these the HCl was nominally 1 molar (in three cases, 0.5 molar). The formulated molar ratio of $FeCl_2$:$FeCl_3$ varied from 10:1 to 1:10. Approximately 240 milliliters of the electrolyte was put into the cell before a set of electrochemical determinations was made, and argon gas was continuously and gently bubbled through the solution before and during the measurements.

In each electrolyte, steady-state anodic and cathodic currents (I) were measured against the reference SCE potential by using a commercial potentiostat. These measurements were made at RDE velocities (ω) of 3.75, 15, and 60 rotations per second. For each solution the ohmic resistance between the RDE and reference electrode well was determined by a current step method. (A circuit consisting of the RDE and counter electrode in series with dry cells and resistances was opened or closed by a mercury-wetted relay, and electron oscillograms were made of the instantaneous change in potential between the RDE and reference well. From the measured current and potential steps the desired resistance was computed.) This resistance (which was found to be reasonably independent of disk current (I)) was used to correct the measured potential for I·R drop. The chemically limited currents were then determined from the I·R-corrected currents by linear extrapolation of plots of I^{-1} against $\omega^{-1/2}$ to $\omega = \infty$. Tafel plots were then constructed from the chemically limited currents.

To help characterize the RDE surfaces, continuous rapid triangular wave voltammograms were made, and the disk was visually inspected through a low-power binocular microscope.

RESULTS AND DISCUSSION

Early in this work, we found that the ohmic I·R drop limits the measurements to current densities of about 100 milliamperes per square centimeter or less. Above this value, accurate values of the electrochemically controlled polarization (η) cannot be obtained.

An example of the polarization data and Tafel plot for one FeII-FeIII solution is shown in figure 1. The data points have been corrected for I·R drop. The electrochemically limited anodic and cathodic Tafel plots ($\omega = \infty$) are shown at the right.

The electrochemical results are summarized in table I. The compositions of the solutions, rest potentials, Tafel slopes b, exchange current densities i_0, and standard rate constant k_s are in chronological order and are for two rotating disk electrodes (RDE I and RDE II) that had initially the same type of mirrorlike finish.

The experimental rest potentials E_0 were found to be consistently less electropositive (by 0.08 to 0.11 V) than their theoretical Nernst potentials from formulated FeII-FeIII concentrations and free energy data. This same trend has been found in work done elsewhere (refs. 5 and 6) at lower concentrations as well as in recent ERDA/NASA contract work at total concentrations of 1 to 4 molar (ref. 2).

These less electropositive rest potentials are consistent with the notion that FeIII forms complexes with Cl^- (or certain other anions (e.g., sulfate) if present in sufficient concentrations). Indeed, Popoff and Kung in 1929 (ref. 7) clearly showed that increasing $[Cl^-]$ can shift E_0 to significantly less electropositive values. The shift of 0.1 volt, found in this work (and by others), indicates that in the electrolytes studied the effective ion concentration ratio $[Fe^{+++}]/[Fe^{++}]$ is an order of magnitude less than the formulated concentration ratio [FeIII]/[FeII]. From the stability constants that are sparsely available for complexes of Cl^- with both Fe^{+++} and Fe^{++} (ref. 8, p. 280) this order of disparity does seem to be possible. Furthermore, as the [FeII]/[FeIII] ratio increases (table I), the negative difference in E_0 increases; such a result could show that $FeCl_2$ yields Cl^- to complex with Fe^{+++}.

Most of our Tafel slopes, b, (table I) are roughly in the region 0.12 volt per decade, which would be expected for a limiting single-electron exchange. In some cases a second Tafel region was found (see fig. 1).

To compare exchange currents, i_0, for different nominal molar concentrations, $[FeCl_2]$ and $[FeCl_3]$, we have calculated standard rate constants

$k_s = i_0[FeCl_2]^{-1/2}[FeCl_3]^{-1/2}F^{-1}$, F being the Faraday (ref. 9, p. 164). The first rotating disk electrode (RDE I) gave initial k_s values of 1.0×10^{-4} centimeter per second when run with iron solutions from 1 to 3 molar in which the molar ratio of FeIII:FeII varied from 2.0:1 to 0.1:1. These initial determinations on one current collector showed that large changes in composition of iron solution had little effect on k_s. Such a result is not surprising when one consideres that k_s is defined in terms of equilibrated (or quasi-equilibrated) reactions (Randles, ref. 10). One must remember that the k_s values as determined from our data (table I) and from others (table II) are not corrected for the effects of complexing. Performance suddenly increased, however, while RDE I was being run in 0.1:0.1 molar FeII-FeIII. After being repolished, RDE I still showed high k_s values, 6×10^{-4} and 5×10^{-4} centimeter per second, respectively, in 0.1:0.1 and 1.4:1.4 molar FeII-FeIII. We hoped to determine more exactly the cause of this transition to higher performance; therefore, a second rotated disk electrode (RDE II) was polished and further determinations were made. With RDE II, the k_s values ranged from 1.0×10^{-4} to 3.4×10^{-4} centimeter per second and did not go higher.

Figure 2 shows voltammograms (made under identical sweep conditions) of both electrodes in 1 molar HCl after all polarization runs on each had been completed. From the enclosed area, the overall activity of RDE I is concluded to be significantly higher than that of RDE II. Voltammograms consistently showed an oxidation peak at about 0.45 volt (referenced to SCE) for RDE I in HCl. This perhaps indicates some surface-held iron. No such peak is seen with RDE II. Microscopic inspection showed RDE I to have a uniform finely cratered surface that RDE II did not have.

We interpret our k_s results to show the existence of two regimes (A and B) of electrochemical efficiency for FeII-FeIII redox on EOPG, that is, k_s (A) - 1×10^{-4} to 3×10^{-4} centimeter per second, and k_s (B) - 5×10^{-4} to 6×10^{-4} centimeter per second. This trend is also suggested by the overall comparison of the work of others in table II. Most of the k_s values (from five separate studies) of several forms of carbon fall in regime A. Aleya and Austin (ref. 5) show that basal planar surface of pyrolytic graphite to give a k_s in regime A and an edge-on surface, a k_s in regime B. Our work shows edge-on surfaces to perform in both the regimes and regime B behavior to result from a permanent modification of the edge-on surface. Our evidence, albeit tenuous, suggests not only that an increase in this surface area has occurred, but also that some iron has become part of the active surface. To date, we have not reproduced this modification (which was observed only with RDE I).

Regime B (table II), however, may not be the ultimate that can be achieved in the redox of FeII-FeIII on carbon. From voltammetric data, Taylor and Humffray (ref. 11) report k_s values that were temporarily as high as 57×10^{-4} centimeter per second on specially treated glassy carbon. Although these high electrochemical efficiencies (ref. 11) did not persist for more than several minutes at continuously cycling potentials, we are hopeful that carbon can be improved as a redox current carrier.

In practical terms, we conclude that

1. Increasing concentration per se in the $FeCl_2$-$FeCl_3$ redox system does not drastically change electrochemical parameters such as k_s and rest potential, albeit the latter is less electropositive than one would expect from free energies and formulated FeII-FeIII concentrations, if complexing is ignored.

2. The limit on current density is expected to be due to I R drop, not electrochemical polarization.

3. The electrochemical efficiency of carbon hopefully might be increased.

From the more basic standpoint, it is understandable why no definitive experimental work in steady-state mechanistics has been reported at concentrations above 0.1 molar. The need for I·R corrections is not only a burden but also admits error which increases as larger current densities are approached. The usefulness of a ring and disk electrode combination becomes problematic in highly concentrated reactants, because uneven current distributions result on a disk when current densities are large (due to high activity) with respect to the ohmic conductivity of the electrolyte.

Our results, nevertheless, show that basic electrochemical behavior in the more highly concentrated iron chloride solutions does not significantly differ from what it is at fractional molarities, that is,

1. In most cases, but not always, our first Tafel slopes b imply single-electron exchange reactions to be limiting in 1 to 3 molar iron, as others have found for fractional iron molarities.

2. With respect to current density i_0, the 1 to 3 molar iron solutions show activities effectively proportional to the formulated concentrations of FeII and FeIII.

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TABLE I. - EXPERIMENTAL RESULTS

Formulated composition, moles/liter			Rest potential, V ref. SCE		Tafel slope b, V/decade		Exchange current density, i_o, $\frac{mA}{cm^2}$	Standard rate constant, k_s, $\frac{cm}{sec}$ $(\times 10^4)$
$FeCl_3$	$FeCl_2$	HCl	Experimental	Difference from theory	Anodic	Cathodic		
EOPG RDE I								
2.0	0	0.50	0.65	------	0.12 ----	0.06 09	0.31 .56	---- ----
2.0	0.10	0.50	0.527	-0.080	0.13	0.08	4.05	0.96
2.0	1.0	0.51	0.453	-0.094	0.21 .28	0.20 -----	13.5 29.1	0.99 2.2
0.10	1.00	1.00	0.356	-0.113	0.12	0.13	2.7	0.95
0.10	0.10	1.00	0.436	-0.093	0.16	0.15	5.8	6.0
1.43	1.43	0.96	0.438	-0.091	0.09	0.13	6.9	5.0
EOPG RDE II								
0.30	3.00	1.00	0.365	-0.104	----	-----	-----	2 - 3
1.43	1.43	0.96	0.436	-0.093	0.09 ---- ----	----- 0.055 .11	32 14.0 47	2.3 .97 3.4
0.10	0.10	1.05	0.451	-0.078	0.14 .18	0.12 .17	0.97 1.63	1.00 1.68

TABLE II - TWO REGIMES OF ELECTROCHEMICAL EFFICIENCY FOR FeII - FeIII ON CARBON

Experimental conditions	Regime	
	A^a	B^b
	Standard rate constant, k_s, cm/sec ($\times 10^4$)	
Graphite paste RDE in <0.2 M Fe; $[Cl^-]$ and $[ClO_4^-]$ varied (ref. 12, 1963)	0.9 - 2.3	-----
Pyrolytic graphite RDE in ~2 M Fe in HCl (ref. 5, 1973)	[c]1.5	[d]5.2
Spectral graphite in 10^{-3} to 0.4 M Fe in H_2SO_4 (ref. 6, 1975)	0.9 - 1.7	-----
Vitrous carbon in 1 to 4 M Fe in HCl (ref. 2, 1976)	1.2 - 2.4	-----
Edge-on pyrolytic RDE in 0.2 to 3 M Fe in HCl (this work, table I)	[e]0.9 - 3.4	[f]5 - 6

[a] $k_s \sim 1 - 3\times10^{-4}$.

[b] $k_s \approx 5 - 6\times10^{-4}$.

[c] Basal planar pyrolytic graphite.

[d] Edge-on pyrolytic graphite.

[e] Newly polished electrode.

[f] Modified electrode.

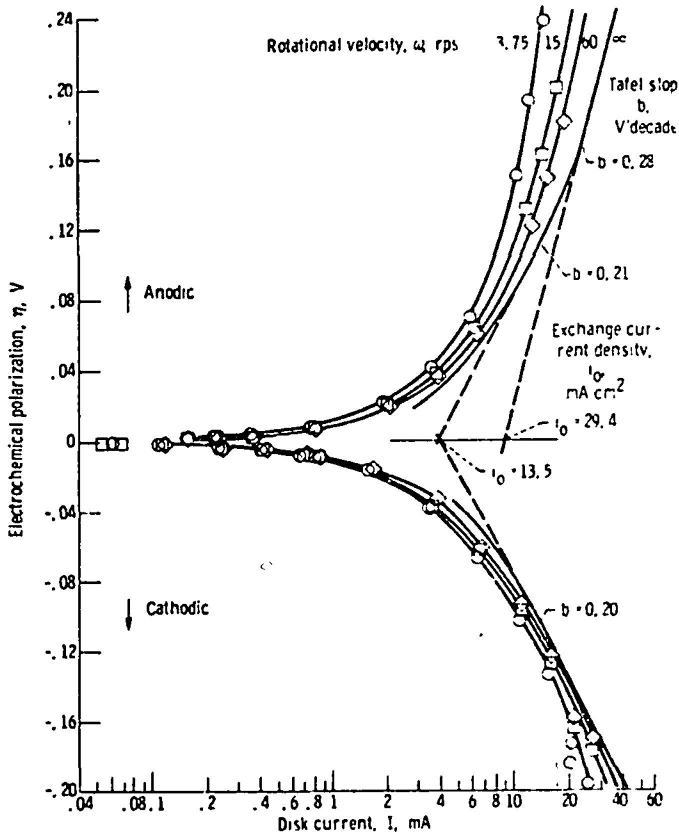
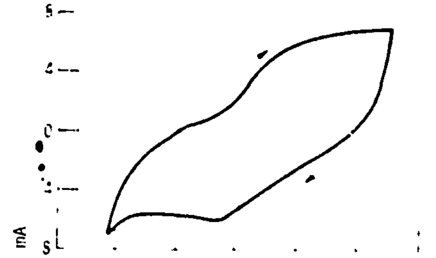
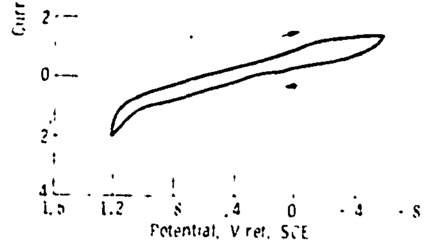


Figure 1. - Polarization data and Tafel plot for 1 molar $FeCl_2$ and 2 molar $FeCl_3$ in 0.5 molar HCl. Edge-on pyrolytic graphite; area of disk, 0.32 square centimeter.



(a) EOPG RDE I.



(b) EOPG RDE II.

Figure 2. - Voltammograms, continuous triangular waves, 2 volts per second 1 molar HCl.