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SU-MOON PARK

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW MEXICO

ALBUQUERQUE, NM 87131

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ABSTRACT

In Task 1, the literature search completed on electrochemical studies of various carbons. Two conclusions reached from this literature search are as follows: 1) The surfaces of various carbons are covered by oxide films to different extents and the oxides resemble either the quinone-like structure in their oxidized form or the hydroquinone-like structure in the reduced form. 2) When carbonaceous materials are oxidized chemically, electrochemically, or thermally, most of the charge is used for the formation of the oxide film in its earlier stage and for the oxide gas (CO or CO_2) evolution in later stages.

In Task 2, the catalytic reaction mechanism of coal oxidations was substantiated by adding Fe^{3+} or Ce^{4+} to the cell containing a coal slurry without passing any electrical current and by monitoring the amount of CO_2 evolved. Also, studies were performed on current efficiencies of the CO_2 production reaction as a function of the particle size of coal samples. Finally, the catalytic rate constants of various redox catalysts for the coal oxidation reaction are reported. These results indicate that thermodynamics of reaction systems plays a predominant role in determining the rate constants.

In Task 4, methods of studying the stability of semiconductor electrodes were established employing rotating ring-disk electrode techniques. The long-term stability of semiconductor electrodes would be needed to carry out the photoassisted coal gasification reaction. In the method we developed, the semiconductor was used as a disk electrode while the noble metal, e.g., Au or Pt, is used as a ring electrode. The species generated at the semiconductor electrode by light illumination is detected at the ring electrode by applying proper electrode potential. If the ring detection current is lower than its expected value, the disk may undergo the photocorrosion reaction.

TABLE OF CONTENTS

	Page
Notice, Patent Status, Technical Status	i
University-Type Contractor's Recommendation for Disposition of Scientific and Technical Document	ii
ABSTRACT	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	v
LIST OF FIGURES	v
I. INTRODUCTION	1
II. Task 1. Electrochemistry of Carbonaceous Materials and Coal -- Literature Review, Part 1	2
A. Electrochemistry of Various Forms of Carbon	2
B. References	9
III. Task 2. Mechanisms of Coal Oxidation	11
A. CO ₂ Increase -- San Juan Coal + Fe ³⁺	11
B. Current and CO ₂ Production vs. Time -- Pennsylvania Coal	11
C. Effects of Fe ³⁺ Addition on CO ₂ Production Rates -- Pennsylvania Coal	15
D. Addition of Ce ⁴⁺ to San Juan Coal -- Current and CO ₂ Evolution Rates vs. Time	15
E. Particle Size vs. Current and Efficiency with Time -- San Juan and Pennsylvania Coal	18
F. Coal-Oxidant Reaction Rates	28
G. References	32
IV. Task 3. Photoassisted Coal Gasification	34
V. Task 4. Stability of Electrode Materials for Photoassisted Coal Gasification	34
A. Introduction	34
B. Experimental	35
C. Results	38
D. Discussion	53
E. Conclusion	53
F. References	54

LIST OF TABLES

Table No.		Page
I	Comparison of Physical Parameters	19
II	Catalytic Rate Constants	31

LIST OF FIGURES

Figure No.		
1	Effects of Fe^{3+} Addition on CO_2 Production -- San Juan Coal	12
2	Electrolytic Currents and CO_2 Current Efficiency vs. Time, Pennsylvania Coal	13
3	CO_2 Production Rates vs. Time under Various Experimental Conditions	14
4	Rate of CO_2 Production Before and After the Addition of Fe^{3+}	16
5	Currents and Current Efficiencies vs. Time with Fe^{3+} and Ce^{4+} Additions	17
6	Currents and Current Efficiencies vs. Time, 40-50 mesh, Pennsylvania Coal	20
7	Currents and Current Efficiencies vs. Time, 140-170 mesh, Pennsylvania Coal	21
8	Currents and Current Efficiencies vs. Time, 230-270 mesh, Pennsylvania Coal	22
9	Currents and Current Efficiencies vs. Time, 40-50 mesh, San Juan Coal	23
10	Currents and Current Efficiencies vs. Time, 140-170 mesh, San Juan Coal	24
11	Currents and Current Efficiencies vs. Time, 230-270 mesh, San Juan Coal	25
12	Limiting Oxidation Current vs. Time at Pt Electrode ($\sim 10 \text{ cm}^2$)	28
13	Current vs. Potential for $\text{Fe}(\text{CN})_6^{4-}$ in Different Media	33
14	Experimental Set-up for Photoanodic Dissolution Studies ...	37
15	Linear Scan Voltammetry of $\text{K}_4\text{Fe}(\text{CN})_6$ at a Rotating Gold Disk-Platinum Ring Electrode	39
16	Effect of pH on the Corrosion Current of an n-CdS Electrode	41

Figure No.		Page
17	a. Cyclic Voltammogram of the Iron(II)-EDTA Complex	43
	b. Cyclic Voltammogram of the Iron(II)-EDTA at an Illuminate n-CdS Electrode	43
18	Photocurrent Spectra at an RRDE	44
19	Effect of the Disk Current on % Corrosion Current for an n-CdS Electrode	46
20	Effect of the Applied Potential on the Photoanodic Dissolution Current for an n-CdS Electrode	47
21	Effect of the Increase in $[\text{Fe}^{2+}]$ on Corrosion Current of an n-CdS Electrode	48
22	Effect of the Concentration of the Supporting Electrolyte Concentration	51
23	Plot of $[\text{Fe}^{2+}]$ vs. Ionic Strength at the Point of Minimum Corrosion	52

I. INTRODUCTION

During the third quarter (January 1, 1982-March 31, 1982) of the current contract, we have been continuing the literature search (Task 1) and detailed studies on coal oxidation mechanisms (Task 2), and also carried out detailed studies on the electrode stability of n-CdS (Task 4).

In Task 1, we collected most of the articles about electrochemical studies on carbonaceous materials and coal and began to analyze the literature. In reviewing this subject, we felt that we can classify it into several categories: 1. electrochemistry of various forms of carbon; 2. chemical oxidation or reduction of coal; 3. electrochemical oxidation or reduction of coal; 4. photo-electrochemistry of coal or carbons; and 5. direct power generation from fuel cells using coal as a fuel. Of these, we report the first portion of the review, i.e., electrochemistry of various forms of carbon.

In Task 2, we carried out more in-depth studies on the anodic oxidation of coal employing various techniques. Various experimental results point to the fact that coal is indeed oxidized by the catalytic process with Fe^{3+} , which has been generated at the electrode by heterogeneous electron transfer. We also report results obtained for the current efficiencies for CO_2 production performed on samples of various particle sizes.

In Task 4, we studied the electrode stability of n-CdS electrodes without coal being photoelectrolyzed. We performed this study to establish the methodology of testing stabilities of semiconductor electrodes under the operating conditions. We believe that the methodology used here can be applicable to the other semiconductor materials.

We have not yet initiated the work on Task 5 since we do not fully understand processes that will be studied under Tasks 3 and 4 in detail. Detailed discussion on results that we obtained during this quarter follows:

II. Task 1.

Electrochemistry of Carbonaceous Materials and Coal -- Literature Review, Part 1.

Since comprehensive reviews of electrochemistry of inorganic¹ or organic² derivatives of carbon compounds have been compiled in the literature, we will limit our report to the electrochemistry of carbonaceous materials relevant to that of coal. In reviewing the subject, we classify it into several categories: 1) electrochemistry of various forms of carbon, 2) chemical oxidation or reduction of coal or carbons, 3) electrochemical oxidation or reduction of coal, 4) photoelectrochemistry of coal and carbons, and 5) direct power generation from coal burning fuel cells. In the current report, only the first subject will be reviewed.

A. Electrochemistry of Various Forms of Carbon.

The oxidation of carbonaceous materials has been studied mainly for two purposes, to characterize surfaces of various carbons and to characterize carbon as an electrode material. We will review these two subjects in this section.

Surfaces of carbon black particles were characterized electrochemically by subjecting them to the polarographic experiment as a suspension in N,N'-dimethylformamide (DMF) as a solvent with 0.1 M tetra-n-butylammonium perchlorate (TBAP) as a supporting electrolyte.³ The limiting current was observed with the half-wave potential ($E_{1/2}$) ranging $-0.58 \sim -0.78$ V (vs. Hg pool) depending on the supporting electrolyte used. When carbon black was treated by strong reducing agents such as lithium aluminum hydride, the polarographic wave was not observed any more. This treated sample, however, gave an anodic wave at about +1.0 V (vs. Hg pool) indicating that oxidizable surface species has been produced upon treatment. This anodic wave disappeared when the

sample was treated with oxidants such as hydrogen peroxide (H_2O_2). From these electrochemical results along with infrared (ir) spectroscopic results, Hallum and Drushel suggested that benzoquinone-like surface groups are responsible for the reduction current. Later, these authors⁴ estimated the amount of quinone oxygen and hydroquinone hydroxyl groups on the surface of carbon blacks by controlled potential coulometric reduction or oxidation. The benzoquinone content ranged $0.002 \sim 0.26\%$; the hydroquinone content was $0.016 \sim 0.47\%$ depending on the sample. These observations were later substantiated by Jones and Kaye⁵ using polarographic methods with a stirred aqueous suspension of activated charcoal.

Mamantov et al.⁶ have shown that electrochemical anodization or chemical oxidation with strong oxidants such as Ce(IV) results in the formation of a film on the surface of pyrolytic graphite. The anodized sample gave a broad cathodic voltammetric peak at about $+0.5 \text{ V vs. SCE}$ ($E_{p/2} = +0.48 \text{ V vs. SCE}$) whereas a sharp oxidation peak was observed at approximately $+0.5 \text{ V vs. SCE}$, which was followed by a broad peak at $\sim 0 \text{ V}$. The authors suggested electrolytic lamellar compounds of graphite as a possibility. In this study and the ones described below, the carbonaceous material was used as an electrode as opposed to the previously described studies, in which a mercury electrode was used in a suspended solution of carbons.

Kinoshita and Bett employed the cyclic voltammetric method to detect surface oxides on carbon black (Vulcan XC-72) which had been subjected to heat treatment, electrochemical and chemical oxidation and also gas phase oxidation. These investigators used a carbon black with a surface area of $220 \text{ m}^2/\text{g}$, which was fabricated using small quantities of Teflon (Dupont), $\sim 10\%$ by weight. The test was made after the carbon black is oxidized or heat treated under various

conditions. The quinone-hydroquinone redox sample was observed in the potential range of 0.05 ~ 1.28 V vs. NHE. Surface concentrations of $10^{-10} \sim 10^{-11}$ moles/cm² of quinone oxides were estimated. The results indicate that various oxidation procedures increase the amount of surface oxides whereas heat treatment at 2000°C and 2700°C decreases the surface oxides. This is because the oxides desorb from the surface as CO upon heat treatment. Blurton⁸ reported similar but much better defined voltammetric peaks using graphite electrodes in 1 N H₂SO₄ solution. A maximum of 3 anodic and 3 cathodic peak currents were observed depending on the experimental conditions. Two peaks at lower potentials showed reversibility at slow scan rates up to about 10 mV/s while the peak separation becomes larger at higher scan rates, indicating a sluggish electron transfer. The author attributed anodic currents to the oxidation of hydroquinone-like surface species and cathodic currents to the reduction of quinone-like groups in different environments.

Observations made by these investigators indicate that 1) carbon surfaces are covered with quinone-like and hydroquinone-like functional groups, which are electroactive and thus give polarographic or voltammetric currents, 2) concentrations of these groups are estimated to be $10^{-10} \sim 10^{-11}$ moles/cm² or up to 0.26% benzoquinone and 0.47% hydroquinone by electrochemical methods, 3) the surface concentrations of these groups are increased upon mild anodic, chemical, or air oxidations, and 4) these groups desorb upon heat treatment as carbon oxides. This information gives an insight into the oxidation mechanism of carbons and graphites as will be discussed immediately below.

Probably the most comprehensive study on the anodic oxidation of various carbons including graphitized active carbon, charcoal, soot, and graphite was carried out by Binder et al.⁹ They employed the current-potential curves, chronopotentiometric measurements, volumetric determination of the product CO₂,

chemical analysis, x-ray analysis, and the electrical resistance as their techniques while the electrode is polarized. From these studies, they concluded that when the electrode potential is lower than the oxygen equilibrium potential, about 80% of the charge is used for oxidation of the carbon electrode to CO_2 and about 20% for the surface oxide formation. They ran these experiments in H_2SO_4 or H_3PO_4 medium and the results appear to be relatively independent of the medium and temperature.

Several other groups of investigators reported the chronopotentiometric (galvanostatic) behavior of various carbon electrodes.¹⁰⁻¹² These investigators report that the electrode potentials level off at several values before they reach the sharply increasing potentials upon application of constant anodic currents. These results indicate that the carbon surface becomes oxidized at several different potentials to different surface species, which is consistent with previously reviewed reports (above) in which mainly the surface characterization has been made.

Kokhanov and Milova¹³ reported the product distribution of oxidations of graphite electrodes in phosphate buffer solutions as a function of pH. These investigators employed the current density of 3.7 mA/cm^2 and monitored the electrode potential as well as the product gas composition. At lower pHs than about 6.7, the current efficiency (CE) for the CO_2 production was ~91% with about 6% for CO and 3% for O_2 . When the pH was increased from 6.7 to 13.0, the CO_2 content gradually decreased down to 5% whereas oxygen productions increased to 95%. The CO product went down almost to nil. At higher pH than 13, the gas composition remained almost the same.

This observation was substantiated by another group of investigators employing polyethylene impregnated graphite electrodes.¹⁴ These investigators performed quite comprehensive studies employing different current densities.

Using log of current densities of -1.5, -2.0, -3.0, -4.0, and -5.0 (unit = mA/cm^2), they classified three potential-pH domains and four regions of different types of oxide surface production.

The electrochemical oxidation of a high surface area carbon black ($1000 \text{ m}^2/\text{g}$) was investigated by Kinoshita and Bett¹⁵ in 96% H_3PO_4 at 135°C . The total anodic current, the amount of CO_2 evolved and the oxygen content at the carbon surface were measured as a function of time and potential. Their results indicate that two anodic processes occur: the formation of a surface oxide and the evolution of CO_2 . The rates of both processes decrease with time but at different rates so that the CO_2 evolution becomes the major reaction in later stages of electrolysis. The current efficiency (CE) for the CO_2 evolution can be expressed by an equation,

$$\text{CE} = \frac{1}{1 + Q_{\text{ox}}/Q_{\text{CO}_2}}$$

where Q_{ox} is the charge used for the surface oxide formation and Q_{CO_2} is for the CO_2 evolution. The charge for the CO_2 evolution was measured by determining the amount of CO_2 assuming that CO_2 production requires a four electron process.

At all potentials the formation of surface oxides is the predominant processes at the beginning of the electrolysis, whereas CO_2 formation predominate in later stages of electrolysis. Thus, the current efficiency for CO_2 production approaches unity as the ratio $Q_{\text{ox}}/Q_{\text{CO}_2}$ approaches zero. The current efficiency for CO_2 production approaches unity more rapidly at higher applied potentials at the anode. These investigators summarized their observation as follows:

- a) Two processes occur initially; surface oxide formation and CO_2 evolution. As the rate of surface oxide formation decreases, CO_2 evolution becomes the major anodic process,
- b) The two processes are independent. The surface oxide does not inhibit CO_2 formation,

- c) The surface oxide coverage approaches, but is less than, a theoretical monolayer, and continues to grow even after CO_2 is the major product, and
- d) The dissolution rates of carbon black electrodes are independent of water concentration, or CO_2 pressure.

The electrode reaction kinetic parameters were studied by several groups of investigators by following Tafel relationship between current and potential.^{14,16-18} In general, Tafel slopes are dependent on the pH of the medium indicating different mechanisms are at work. Most of these investigators used the galvanostic measurements at various carbon electrodes.

Not much attention has been paid to the mechanism of CO production from the carbon oxidation mainly because of the lower fraction of it in the product composition. It appears that the desorption of oxides occurs in the form of CO in gaseous state under vacuum.⁷ In the aqueous solution, CO_2 appears to be a major product with a few percent of CO detected.¹⁰ When the amount of CO_2 produced becomes sizable, the Boudouard reaction in pores behind the electrode surface,

may occur producing a small amount of CO as a product.¹⁹ Thus, CO may be produced only if a large electrolysis current is passed.

Studies reviewed thus far were concerned with the electrochemical behavior of carbonaceous material either in suspension at Hg electrodes or as an electrode in a buffered solution that is not electroactive itself. Many investigators, however, studied electrochemical corrosion of graphite anodes in aqueous chloride electrolytes²⁰⁻²² or while electrowinning aluminum.¹⁹ The basic processes occurring under these environments are similar, but reaction

mechanisms are more complicated due to the generation of oxidants such as OCl^- , ClO_3^- , etc. The reader should consult references cited for these studies.

Summarizing this section, we can conclude that the oxidation of various carbons occurs through two pathways: formation of surface oxides and CO_2 evolution. These two reaction pathways were claimed to be independent of each other by Kinoshita and Bett.¹⁵ It appears, however, that they may not be independent of each other. Although not proved, it would be reasonable to suggest that the formation of surface oxide precedes the CO_2 evolution reaction. When all the surface is covered with oxide film, the oxide desorbs as CO under vacuum and as CO_2 with water present as electrolysis goes on. This is evident even in Kinoshita and Bett's data; the current efficiency of CO_2 evolution increases with the electrolysis time.

Although the mechanism for carbon oxidation is not well understood, one can readily conclude that the electron transfer reaction does not include the water molecule, proton, or hydroxide ion. If the stoichiometry,

correctly represents the carbon oxidation, the electrode potential would be pH-dependent and thus, the product distribution should remain independent of pH. Actually the oxygen evolution

becomes predominant at higher pHs indicating that the electrode potential of this reaction shifts upon changes in pH as predicted by the Nernst equation. Potentials monitored during the galvanostatic electrolysis of polyethylene impregnated graphite decreased from about +1.6 V at pH = 1.0 to about 0.70 V at pH = 14.5.¹³ Thus, the electrode potential is controlled by the carbon oxidation at low pHs where oxygen overvoltages are high; the oxygen evolution reaction determines the electrode potential in higher pH regions.

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III. Task 2. Mechanisms of Coal Oxidation

To prove the mechanism we proposed in our earlier reports on the anodic oxidation of coal, we ran further experiments in which oxidants such as Fe^{3+} or Ce^{4+} were added to the solution containing coal slurry without passing electric currents. Also, effects of the coal particle size on oxidation currents as well as current efficiencies have been studied and the results are reported. Finally, the catalytic rate constants for oxidation of coal slurry were evaluated and reported for various oxidation catalysts. Coal samples used for this study were one taken from the San Juan Basin, northwestern New Mexico, and one from Pittsburgh Seam #8 (PSOC-1099) obtained from Pennsylvania State Coal Sample Bank and Data Base, Coal Research Section, Pennsylvania State University, University Park, Pennsylvania.

A. CO_2 Increase -- San Juan Coal + Fe^{3+}

If the reaction of coal with Fe^{3+} is a continuing process and not due to some initial reaction which then exhausts some source of CO_2 in the coal, then addition of further Fe^{3+} should give an increase in CO_2 production.

We ran this experiment with unwashed San Juan coal, whose initial burst of CO_2 production was allowed to decrease to a relatively low level. Then, $\text{Fe}_2(\text{SO}_4)_3$ was added to make the 150 ml solution 0.20 M in Fe^{3+} . Results are shown in Figure 1. This experiment should leave no doubt as to the source of the CO_2 produced in these experiments. It is a direct product of the oxidation of the coal by the oxidizing entity (in this case, Fe^{3+}). It should be pointed out that the whole system was not connected to an electrical source; CO_2 is produced purely by chemical oxidation of coal with Fe^{3+} .

B. Current and CO_2 Production vs. Time -- Pennsylvania Coal

In Figures 2 and 3 are plotted the current and CO_2 production vs. time for the Pennsylvania coal with 0.1 M Fe^{3+} in 1 M H_2SO_4 . Also plotted are the CO_2

Fig. 1. San Juan Coal (20 g) in 150 ml 1.0 M H₂SO₄ @ 70°C 0.20 M Fe³⁺ (as Fe₂(SO₄)₃) added at mark indicated. No current. Purge gas N₂ @ 50 cc/min.

Fig. 2. Pennsylvania Coal (20 g) in 150 ml 1.0 M H_2SO_4 + 0.10 M Fe^{3+} @ 70°C Current and CO_2 Production Efficiency versus Time. Potential = +1.0 V vs. NHE @ 10 cm² Pt Electrode. Purge gas N_2 @ 50 cc/min.

Fig. 3. Pennsylvania Coal (20 g) in 150 ml 1.0 M H₂SO₄ @ 70°C CO₂ Production versus Time. Purge gas N₂ @ 50 cc/min.

production rates for Pennsylvanian coal with no current flow, with no Fe^{3+} added and for acid-washed Pennsylvanian coal.

As with the San Juan coal, the CO_2 production rate increases when oxidation current is applied to the system. The increase is not as dramatic as with the San Juan coal, but is none-the-less significant. However, the important parameter is the amount of current passed in the cell. The current passed is initially 30-40 mA, decaying down to a level of a few milliamperes after a few days. This is the same type of behavior seen with the San Juan coal. As with the San Juan coal, efficiency of CO_2 production increases with time of electrolysis. The Pennsylvania coal efficiency increases faster than the San Juan coal, however, and seems to be much more time dependent over-all.

The Pennsylvania coal is a higher order coal than the San Juan coal, and so should contain fewer reactive functional groups. The reactive functional groups will be depleted faster and thus the remaining oxidations will be more efficient in producing CO_2 . This may account for the greater increase in efficiency for the Pennsylvania coal vs. the San Juan coal.

C. Effects of Fe^{3+} Addition on CO_2 Production Rates -- Pennsylvania Coal

We ran the same type of experiment with Pennsylvania coal that we had run with San Juan coal, adding the Fe^{3+} to coal whose CO_2 production rate had been stabilized. Figure 4 shows the results. Once again, addition of Fe^{3+} increased the amount of CO_2 produced on the cell, although not as drastically as for the San Juan coal. This again may indicate the dearth of reactive functional groups on the Pennsylvania coal compared to the San Juan coal.

D. Addition of Ce^{4+} to San Juan Coal -- Current and CO_2 Evolution Rates vs. Time

As a comparison with the experiment on CO_2 production and efficiency vs. time for San Juan coal with Fe^{3+} added, we ran an experiment under the same conditions utilizing 0.1 M Ce^{4+} . In Figure 5, one can see the current and efficiency vs. time for this system. The amount of CO_2 produced was 5-10 times

Fig. 4. Pennsylvania Coal (20 g) in 150 ml 1.0 M H₂SO₄ @ 70°C 0.20 M Fe³⁺ (as Fe₂(SO₄)₃) added at mark indicated. No current. Purge gas N₂ @ 50 cc/min.

Fig. 5. San Juan Coal (20 g) in 150 ml 1.0 M H_2SO_4 + 0.10 M $[\text{M}^{n+}]$ @ 70°C. Current and CO_2 Production Efficiency versus Time. Potential + 1.00 V vs. NHE for Fe^{3+} , + 1.50 V vs. NHE for Ce^{4+} , at 10 cm² Pt electrode. Purge gas N_2 @ 50 cc/min.

larger than with Fe^{3+} . This increased rate of CO_2 production seems to reflect the increased rate of reaction of coal with Ce^{4+} which has been seen in the rate studies.

For comparison purposes the current and efficiency vs. time for San Juan coal + Fe^{3+} have been included in this figure. It is immediately apparent that the rate of reaction of Ce^{4+} with coal is much greater than Fe^{3+} . Also, one may note the larger final efficiencies of CO_2 production achieved with Ce^{4+} . The Ce(IV) is apparently able to totally oxidize (i.e. to CO_2) functional groups more readily than Fe^{3+} can resulting in more efficient CO_2 production. This conclusion is also supported by the current vs. time curve for Ce^{4+} compared to Fe^{3+} . The iron(III) curve shows an initial high current, but drops off rather rapidly as the more easily oxidizable species on the coal surface are used up. Cerium (IV), on the other hand, maintains a high current for a much longer period, and thus shows an ability to react with functional groups which do not react well with iron(III).

E. Particle Size vs. Current and Efficiency with Time -- San Juan and Pennsylvania Coals.

Farooque and Coughlin ran a set of current vs. time with particle size experiments for their coal.¹ However, there is a fallacy in their experiments based on what we now understand about the nature of the coal oxidation reaction. The amount of iron in various particle size fractions of a coal may vary considerably due to differences in the amount of the iron ion leached out.

Farooque and Coughlin's results may simply represent the variation in current for differing amounts of solvable iron in the various slurries they tested. In order to remove this variable, we decided to run a set of tests using a large excess of iron(III) to eliminate any effects seen from natural iron. Our experiments were run with 5 g of the appropriate size fraction of coal in 150 ml of 1 M H_2SO_4 containing 0.20 M Fe(III) at 70°C. The particle sizes used were 45-50

mesh, 140-170 mesh and 230-270 mesh.

These experiments were run to determine the effect, if any, of particle size on the reaction rate of the coal. If one can achieve an increase in reaction rate simply by increasing the surface area of the coal, this may eliminate the need for developing catalysts or faster oxidation agents for the coal.

In Table I, we list the calculated parameters for different mesh sizes of coal, based on spherical particles.

Table I. Comparison of Physical Parameters.

Mesh Size	Diameter of Particles (cm ²)	Average (cm ²) Particle Area	Average (cm ³) Particle Volume	Area per Weight vs. 45-50 mesh
45-50	0.035-0.030	3.3×10^{-3}	1.8×10^{-5}	1
140-170	0.0105-0.0088	2.9×10^{-7}	4.7×10^{-7}	3.37
230-270	0.0062-0.0053	1.0×10^{-4}	1.0×10^{-8}	5.49

These experiments were run for about 100 hours each, giving not only the initial reaction rates (i.e. oxidation currents), but the currents after some period of time. The current efficiency of CO₂ production was also measured, as before, by purging the cell with N₂ and measuring the spectrum of the effluent gas by FTIR. As in all other experiments we have run up to now, no CO was seen in the effluent gas stream.

Figures 6-11 show the current and current efficiency vs. time for the different particle sizes of San Juan (Figs. 9-11) and Pennsylvania coal (Figs. 6-8). Of the two coals, the San Juan data (Figs. 9-11) is the easier to interpret. The initial current increases with decreasing particle size, a fact consistent with a reaction rate dependent on how much of the coal surface is exposed to the solution. The initial fast rise in iron(II) oxidation current indicates a fast process with which the electrode reaction cannot keep up. This phenomenon is

Fig. 6. Pennsylvania Coal: 45-50 mesh (5.0 g) in 150 ml 1.0 M H_2SO_4 + 0.20 M Fe^{3+} @ 70°C. Potential = +1.00 V vs. NHE at 10 cm² Pt electrode. Purge gas N_2 @ 50 cc/min. Current and CO_2 Production Efficiency versus Time.

Fig. 7. Pennsylvania. Coal: 140-170 mesh, same as Fig. 6.

Fig. 8. Pennsylvania Coal: 230-270 mesh, same as Fig. 6.

Fig. 9. San Juan Coal: 45-50 mesh, same as Fig. 6.

Fig. 10. San Juan Coal: 140-170 mesh, same as Fig. 6.

Fig. 11. San Juan Coal: 230-270 mesh, same as Fig. 6

also seen in other of our studies. This is followed by a drop in current as the readily reactive sites on the coal are used up and the reaction rate drops. Admittedly, some of the current seen initially may be due to iron(II) leached out from coal, but calculations show that not all the current drop is due to depletion of these leached ions.

Note that initially (30 minutes after coal is added to the hot acid) there is a relatively high CO_2 production current efficiency value. This may be due to two effects. The first is the reaction of free carbonates with the hot acid to form CO_2 . This reaction should proceed quickly, and there is some doubt on our part that this reaction would still be producing CO_2 at that time. The other possibility would be that the readily oxidizable groups on the coal, which we postulate are responsible for the sudden rise in iron(II) concentration initially, may oxidize to CO_2 .

The CO_2 production current efficiency then drops through a minimum and increases back to a somewhat stable value which we feel represents the nature of the coal-metal ion reaction. Since the order of the reaction which produces Fe(II) has been shown to be about one with respect to the coal and the metal ion, we believe that not all metal ion reactions with the coal produce CO_2 . Some of the reactions are only partial oxidations which do not immediately lead to CO_2 . Eventually, of course, the surface will become more saturated with these partially oxidized sites, and CO_2 production current efficiency will increase. We believe that we are seeing this at longer times in these tests, when the current efficiency value begins increasing somewhat. Also, note the larger CO_2 production efficiencies for the smallest mesh size of San Juan coal.

The data of the Pennsylvania coal is somewhat more difficult to interpret, although some features are very similar to the San Juan coal curves. Again the iron(II) oxidation current rises quickly and peaks at a relatively high current

value, followed by a drop off to a much lower and fairly stable current. Note that the steady state currents for the Pennsylvania coal are 2-4 times lower than for San Juan coal. We believe, as has been stated above, that this is due to the lesser amount of reactive sites on the higher order coal.

The current efficiency values for CO_2 production again start at an initial high value and go through a minimum. This minimum seems to indicate a phase of the reaction where much oxidation of the coal has occurred without CO_2 generation. This minimum, however, may be due to iron(II) leached from the coal, which has not produced CO_2 but will produce oxidation current for some period after the coal is introduced to the acid.

As with the San Juan coal, the smaller mesh fractions give higher CO_2 production efficiencies. Undoubtedly the smaller particles represent the softer fractions of the coal and as such should produce more CO_2 per oxidation. This indeed seems to be the case, with efficiencies for the Pennsylvania coal running over 100% for the smaller fractions. This is not impossible, as shown in the following argument.

Functional groups on the coal which are already partially oxidized (i.e. quinones) need only one two-electron or two one-electron transfers to produce CO_2 . Our calculation of efficiency is based on four electrons per molecule of CO_2 . If all functional groups which were oxidizing on the coal surface were quinones, the efficiency by our method of calculation would be 200%.

For both coals, higher current seems to be associated with lower CO_2 production current efficiency. It is important to point out that this relationship is not a proportionality, that is, equal amounts of CO_2 being produced for each mesh size with variations in current accounting for the different current efficiency values. This can be easily seen by comparing 230-270 mesh San Juan coal with the other mesh sizes of San Juan coal. Higher steady state current indicates more reactive sites on the coal surface, but lower efficiency

indicates that these sites are not immediately producing CO_2 .

Data from these experiments seems to indicate that some specific functional groups are responsible for the reduction of iron(III) or other suitable oxidizing agent. The findings also show that no great increase in reaction rate can be obtained by using smaller particle sizes of coals. For the Pennsylvania coal, smaller particle sizes give less steady state current.

It must be noted here that the current efficiency of production of CO_2 is not actually very important to the feasibility of the production of H_2 from coal by this electrochemical method, except indirectly as it is the eventual final product. The important parameter is the steady state oxidation current obtained at a reasonable potential.

F. Coal-Oxidant Reaction Rates

One would like to find some redox catalysts with as low a standard potential as possible which would still oxidize coal at a fast rate. This redox pair must also be soluble in water or acid solution to a large extent, stable over a long period of time, have a relatively large heterogeneous electron transfer rate constant at the electrode and be relatively inexpensive. Most importantly, our redox system should be one in which our semiconductor photoelectrode is stable.

In our last report we briefly studied some oxygen-containing oxidizing agents and found that, while they may react with the coal, the reduced form cannot be reoxidized at the electrode at any practical rate. We stated that some complexes of iron may show promise as coal oxidation agents. We have studied iron in the presence of various complexing agents to determine its reaction rate with coal.

In Figure 12 are plotted the oxidation currents monitored at various times for the amount of a reductant produced when an oxidation catalyst is added to the coal slurry. In this experiment, no current is passed except when the measurement is made. Thus the currents shown in the figure indicate the amount

Fig. 12. Washed San Juan Coal (2.0 g) in 75 ml Solutions of Various Oxidants, @ 20°C. Limiting Oxidation Current versus Time @ 10 cm² Pt electrode.

of reductant produced due to the reaction,

One point which is immediately apparent here is that Br_2 and Ce^{4+} by far have the highest reaction rates, and that iron(III) in 1 M H_3PO_4 does not react at all (or very little) with the coal. In these experiments the coal used was acid-washed San Juan coal, with 2.0 g. of coal added to 75.0 ml of the appropriate solution of oxidant at room temperature.

The heterogeneous electron transfer rate constants at the electrode for the different systems used are not identical, so a known concentration (1×10^{-3} M) of the reduced species was measured in the same cell to find the concentration of reduced species per amount of current for each. These values were used to calculate the amount of oxidant reacted with the coal and thus the reaction rate.

In Table II we list the calculated reaction rates and standard potentials for the oxidation systems used. Between 0.44 V and 0.68 V, the reaction rate increases more than ten times. Yet between 0.68 V and 0.77 V, the reaction rate only increases by 1.5-2.0 times. The range between 0.77 V and 1.06 V shows a ~ 50 fold increase in reaction rate, which seems relatively level to +1.45 V (Ce^{4+} shows ~ 20 fold increase over Fe^{3+} in 1 M HCl). These values seem to indicate that some specific functional group or groups are reacting with the oxidants. One of these groups has a potential somewhere around 0.6 volts and one has a potential somewhere around 0.9 volts. All potentials here are referenced with respect to the standard hydrogen electrode (SHE).

Various investigators have found electroactive groups on graphites and carbons used as electrodes. The most common groups appear as oxidation waves at ~ 0.5 - 0.6 volts and at ~ 0.9 volts. These waves have been assigned by various investigators to quinone- and hydroquinone-like groups on the carbons.^{2,3} This oxidation film is also active at the potential which has been determined to be quinoid groups.

Table II. Catalytic Rate Constants.

System	E°	k _c (through first hour) @ 20°C
Fe(III) in 1 M H ₃ PO ₄	0.44	7.2 x 10 ⁻⁷ sec ⁻¹
Fe(III) in 1 M H ₂ SO ₄	0.68	9.6 x 10 ⁻⁶ sec ⁻¹
Fe(III) in 1 M HClO ₄	0.75	1.9 x 10 ⁻⁵ sec ⁻¹
Fe(CN) ₆ ⁻³ in 1 M H ₂ SO ₄	0.69	2.1 x 10 ⁻⁵ sec ⁻¹
Br ₂ in 1 M H ₂ SO ₄	1.06	1.1 x 10 ⁻³ sec ⁻¹
Ce ⁺⁴ in 1 M H ₂ SO ₄	1.45	4.1 x 10 ⁻⁴ sec ⁻¹
Fe(CN) ₆ ⁻³ in sat. K ₂ SO ₄	~0.49	3.6 x 10 ⁻⁶ sec ⁻¹

We now have good reason to believe that coal oxidation proceeds through the oxidation (and perhaps also preceding oxide formation) of quinoid groups.

Note the reaction rate data again. In our last report we mentioned that complexation of iron(III) with ortho-phenanthroline to raise its oxidation potential might produce faster kinetics. Indeed, this may be the case, but the o-phenanthroline complex of iron(III) was found to be too unstable to be suitable for coal oxidation. In rate studies with iron(III) in the presence of o-phen., the reaction rate was found to be no faster than with iron(III) in 1 M H₂SO₄. A much faster reaction rate was found for Fe(CN)₆³⁻ in 1 M H₂SO₄, as well as iron(III) in 1 M HCl and 1 M HClO₄. Part of this effect is probably due to the increased standard potential of iron(III) in HCl and HClO₄. However, complexation must play some role, since Fe(CN)₆³⁻ in 1 M H₂SO₄ had a reaction rate twice as fast as iron(III) in 1 M H₂SO₄ even though the standard potentials for these two systems are virtually identical.

As a test of the effect of complexation, Fe(CN)₆³⁻ was reacted with the

washed coal in saturated K_2SO_4 . The resulting reaction rate is also listed in Table II.

It is much lower than $Fe(CN)_6^{3-}$ in 1 M H_2SO_4 , more on the order of the rate found in iron(III) in 1 M H_3PO_4 . The determining factor here is that in the less acidic solution the standard potential for the ferricyanide/ferrocyanide pair has decreased by about 0.2 volts, now being around 0.49 volts. This can be seen in Figure 13, where the oxidation currents for the two reduced systems are plotted versus potential. The limiting currents are almost identical, but the standard electrode potentials are not. So, while faster kinetics resulting from complexation play some role, the overwhelming determinant of reaction rate in coal oxidation is the standard electrode potential of the oxidant.

G. References

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Fig. 13. Current vs. Potential for $1.0 \times 10^{-3} \text{ M Fe(CN)}_6^{4-}$ in Identical Solutions @ 20°C .

IV. Task 3. Photoassisted Coal Gasification

No significant results have been obtained in this area.

V. Task 4. Stability of Electrode Materials for Photoassisted Coal Gasification

A. Introduction

One of the major problems in constructing photoelectrochemical cells (PEC) for photoassisted coal gasification is the instability of many semiconductor electrodes having small band gaps. The instability of semiconductors in aqueous solutions is widely recognized and studied¹⁻⁷. The long term stability would be required for semiconductor materials to carry out photoassisted coal gasification reactions successfully. The semiconductor materials most often studied include TiO_2 , Si, GaAs, ZnO, and CdS. Many semiconductors are not very stable in aqueous solutions. It appears that the stable semiconductors have large band gaps and thus the conversion efficiencies from light to electrical energy are generally low⁵⁻⁷. It is therefore very important to understand the instability of lower band gap semiconductors in aqueous solutions.

Recently the thermodynamics of stabilities of semiconductor electrodes has been discussed by several authors^{1,8,9}. The arguments may be summarized as follows. When the standard electrode potential (E°) for cathodic dissolution of the electrode material is more negative than the conduction band edge, the electrode should be stable cathodically¹. The electrode is anodically stable if the standard electrode potential for anodic dissolution is more positive than the valence band edge. Even if the anodic dissolution potential is negative of the valence band edge, an n-type electrode may be made stable, provided a redox couple having a lower standard electrode potential than that of the anodic dissolution of the semiconductor is used. The converse is true for a p-type semiconductor material⁸. Pourbaix diagrams have also been used to represent those relations described above in a wide pH range⁹.

Experimentally, a few different approaches have been employed to study the stability of semiconductor electrodes. Methods such as weighing an electrode¹⁰⁻¹² or determining the amount of the dissolved species^{13,14} derived from the electrode material in solution before and after illumination have been used. A more elegant method utilizes a rotating ring-disk electrode (RRDE, as reported by Miller et al.^{15,16}, Inoue et al.¹⁷, and Memming^{18,19}. In this method, one uses a semiconductor disk electrode and a metal ring electrode. For example, electroactive substance (reductant) is oxidized by photoillumination at an n-type disk semiconductor electrode, and an oxidized species photoelectrochemically generated at the disk electrode is monitored at the metal ring electrode by applying an appropriate negative potential to reduce it. If the semiconductor electrode does not undergo a reaction with the photogenerated holes, one observes a collection efficiency expected from the electrode geometry, i.e., dimension of the RRDE^{20,21}. The collection efficiency is defined as

$$\gamma = \frac{i_R}{i_D} \quad (1)$$

where i_R and i_D are the currents observed at the ring and disk electrodes, respectively. The collection efficiency obtained from a semiconductor disk-metal ring electrode will be the same as the one that would be obtained from the metal-metal RRDE or that would be predicted from the geometry of the RRDE, unless the semiconductor electrode is photocorroded. If photocorrosion occurs, the collection efficiency will deviate negatively from the predicted values.

In our current report, we describe our results obtained from a CdS-disk/gold-ring electrode under various conditions.

B. Experimental

Mallinkrodt's Analyzed Reagent (AR) $K_4Fe(CN)_6$, $Fe(NH_4)_2(SO_4)_2$, ethylenediaminetetraacetic acid (EDTA in disodium salt), and Baker's AR NaOH, were

used as received. Mallinckrodt's AR KCl was recrystallized from twice distilled water and used as a supporting electrolyte. All solutions were freshly prepared with twice distilled water before use.

A Pine Instrument (Grover, PA) Model #112 RRDE that had a removable disk electrode was used with a disk CdS electrode. This RRDE had a collection efficiency of 0.24 with a gold disk electrode and a gold ring electrode in a solution containing 1.1×10^{-4} M $K_4Fe(CN)_6$ and 0.50 M KCl at a rotation speed of 500 rpm, which was in excellent agreement with the calculated value from the given geometry. The CdS-disk was attached to the brass disk support by a silver epoxy (Abelbond 36-2, Ablestik Adhesive Company, Gardena, CA). The brass inserts were approximately 3-5 mm shorter than the gold insert so that the disk electrode could be adjusted flush with the RRDE surface. This adjustment was accomplished with the aid of a binocular microscope. The CdS single crystal was obtained from Electronic Space Products (Los Angeles, CA) and cut into disks of 5 mm in diameter to fit the RRDE (area = 0.196 cm^2). The CdS crystal was found to have the donor density of $2 \times 10^{-17} \text{ cm}^{-3}$ as determined by the Mott-Schottky method. The electrode was polished with 10 μ emery paper and gamal polishing cloth, followed by etching with dilute HCl and rinsing well with water and acetone before every experiment. This electrode was used by connecting to a Pine Instrument RDE 3 dual potentiostat. The currents were recorded on either a Houston Model 2000 X-Y recorder or a Houston Omni Scribe strip chart recorder. An Oriel Xenon arc lamp (1000 W), with the Oriel 8540 Universal power supply was used as a light source for illumination. Monochromatic light was obtained from an Oriel 7240 monochromator with a band pass of approximately 20 nm. The pH was monitored by a Cambridge 5-700 combination electrode on a Sargent-Welch Model NX digital pH meter.

The electrochemical cell (Fig.14) had two compartments separated by a fine porosity glass frit. One accommodated an RRDE, a glass electrode for the pH-meter, an SCE reference electrode, and a stopcock-capillary to add the desired

Fig. 14. Experimental Set-up for Photoanodic Dissolution Studies.

concentrated solution; the other compartment contained a Pt-foil counter electrode. The working electrode compartment was constructed with a capability of the bubbling of inert gas such as nitrogen or argon. A flat pyrex glass cell bottom served as an optical window with the electrode being illuminated from below.

C. Results

The RRDE used in this study had a collection efficiency expected from its geometry when a gold disk and a platinum ring electrodes are used. Typical voltammograms at the disk and the ring electrodes using $1.0 \text{ m } \underline{\text{M}} \text{ K}_4\text{Fe}(\text{CN})_6$ are shown in Fig.15. The collection efficiency calculated from the voltammograms was 0.24 irrespective of the disk potential. The collection efficiency calculated from its geometry ($r_1 = 0.250 \text{ cm}$, $r_2 = 0.350 \text{ cm}$, $r_3 = 0.400 \text{ cm}$) using an equation of Alberry and Bruckenstein²² was 0.239. The collection efficiency, however, was found to decrease as a function of the rotation speed due probably to the poor sealing between the removable disk electrode and the teflon gap. This problem was somewhat eased by filling the gap with the Apiezon grease, followed by a thorough polishing and etching procedure. Quite reproducible collection efficiencies were obtained at a constant rotation speed, but the collection efficiency still showed a slight dependency upon the rotation speed. For this reason, we have used the rotation speed of $300 \sim 500 \text{ rpm}$ for this study, in which region the collection efficiency was constant and found to be 0.238.

Since many investigators^{1,15-19} reported the PEC with $\text{K}_4\text{Fe}(\text{CN})_6$ as a reductant for the n-CdS electrode, we also used it in our study. The results, however, showed that very high corrosion currents (73-99% depending on pH; Fig. 16. were observed for the n-CdS disk electrode, in contrast to the results reported by

Fig. 15. Linear Scan Voltammetry of $K_4Fe(CN)_6$ at a Rotating Gold Disk-Platinum Ring Electrode.

Fig. 16. Effect of pH on the Corrosion Current of an n-CdS Electrode.

Ef
n-C

Memming^{18,19}. Memming has reported that 100% of holes generated were consumed to oxidize ferrocyanide between pH = 6 and 13. Heller and Miller^{15,16} showed by their voltammograms at the gold ring and n-CdS disk electrodes that a large portion of holes generated upon illumination are consumed for the oxidation of ferrocyanide up to about -0.65 V vs SCE, but at more positive potentials the ring collection current drops while the disk current rises, indicating a high rate of corrosion. Thus, our results agree well with their results at the disk potential higher than -0.5 V vs. SCE; quantitative comparison is not possible, since they showed only voltammograms at the disk and ring electrodes. Since our measurements were made at the applied potential of 0 V vs. SCE, our results are also in agreement with thermodynamic prediction as well as the recent results using thin film and polycrystalline CdS electrodes²³. The standard electrode potential for the ferro/ferri-cyanide pair is listed as 0.123 V vs. SCE; the formal potential is about 0.47 V in the acidic medium²⁴. The formal potential is definitely higher than the standard electrode potential for the anodic dissolution of CdS (0.08 V vs. SCE), making the process of anodic dissolution of the electrode a major path for hole consumption.

It is interesting to note that the photodissolution current went down as the pH of the medium increased when ferrocyanide was used as a reductant (Fig. 16). The reverse trend, however, would be expected from the Pourbaix diagram. This may be explained by two effects. First, the decrease in pH decreases the effective concentration of Fe(CN)_6^{4-} at low pH through equilibrium reactions

Secondly, due to these reactions, the standard electrode potential for the ferri-/ferro-cyanide pair would be affected. The E° value for ferri-/ferrocyanide becomes pH dependent below about pH = 5.0 and the formal potential (E°') becomes very high

in strongly acidic medium. The E° value is 0.71 V vs. SHE in 1 M HCl. Thus, as the pH increases, 1) more $\text{Fe}(\text{CN})_6^{4-}$ species will be available due to complete dissociation, and 2) the redox potential will approach to the E° value. Similar trend has been reported by Memming, although practically no dissolution currents were observed in his report between pH = 6-13^{18,19}.

Since there were high corrosion currents when ferrocyanide was used as a reductant, we have used the Fe(II)-EDTA complex for most of our experiments. The iron(II)-EDTA complex was prepared by adding an EDTA-disodium salt solution to the solution containing ferrous ammonium sulfate. Since the complex was found to be oxidized by oxygen in the air, the Fe^{2+} -solution was bubbled with nitrogen before the addition of EDTA. The cyclic voltammetric peak potential for oxidation was -0.064 V vs. SCE for this complex at a platinum electrode in pH = 3.8, which would be approximately 30 mV more positive than its standard electrode potential, assuming that its oxidation is reversible (Fig. 17a). Thus, the oxidation potential of this complex is approximately 0.15 ~ 0.20 V more negative than that of CdS. The electrochemical behavior of this complex is shown in Fig. 17 at both a platinum electrode (Fig. 17a) and an illuminated n-CdS electrode (Fig. 17b). With this complex as a reductant, effects of following experimental parameters upon anodic photodissolution currents of CdS have been studied: a) the disk current, b) applied disk potential, c) concentration of the reductant and d) concentration of supporting electrolyte.

Effects of source wavelengths on the CdS-disk current and the collection current at the platinum ring are shown on Fig. 18. The photocurrent spectrum at the n-CdS electrode agrees well with published spectra^{16,25,26}. The reason for the shorter wavelength cut off could be due to the low lamp intensity. Inspection of the photocurrent spectra at the disk and ring electrodes reveals qualitatively that the photoanodic dissolution current at the disk electrode is constant throughout the wavelength region scanned.

Fig. 17. a. Cyclic Voltammogram of the Iron(II)-EDTA Complex
 b. Cyclic Voltammogram of the Iron(II)-EDTA at an
 Illuminate n-CdS Electrode.

Fig. 18. Photocurrent Spectra at an RRDE.

The dependency of the photoanodic dissolution currents on the currents at the illuminated CdS-disk electrode is shown in Fig. 19. The disk currents were controlled by varying the intensity of the incident light. The results show that the photoanodic dissolution current increases at higher illumination intensities. This experiment illustrates that sulfide at the electrode surface competes with the reductant molecules in solution for the holes generated upon illumination. At high illumination intensity, the flux of the reductant molecules toward the electrode surface appears to be a rate-limiting step, enhancing oxidation of the electrode material, CdS, at low concentration.

The potential dependency of the photodissolution currents is shown in Fig. 20. For this measurement, the collection current at the ring electrode was measured while the potential applied at the illuminated CdS-disk electrode varied. We have varied the potential at the disk between $-0.50 \sim 0.0$ V vs. SCE, since very low anodic current flows beyond -0.50 V vs. SCE (Fig. 17b). In this potential range, only the anodic photocurrent for oxidation of the reductant would vary without forcing oxidation or reduction of the electrode material at the pH indicated. Results show that there is no dramatic effect of the applied potential on the photo-dissolution current.

An experiment was carried out such that effects of both increasing concentrations and lowering the standard electrode potential of the reductant solution could be studied. To accomplish this, the concentration of Fe^{2+} was increased, and at a certain concentration of Fe^{2+} , EDTA was added as a complexing agent to lower the redox potential of the solution species. A typical result is shown in Fig. 21. The dissolution current decreased as the concentration of Fe^{2+} increased until it leveled off. When EDTA corresponding to 2.1 mM was added to this solution, the dissolution current dropped drastically. Then further addition of Fe^{2+} to this solution enhanced the corrosion rate slightly. When the concentration of only Fe^{2+} or the iron(II)-EDTA complex was increased similar effects to those shown in Fig. 21

Fig. 19. Effect of the Disk Current on % Corrosion Current for an n-CdS Electrode.

Fig. 20. Effect of the Applied Potential on the Photoanodic Dissolution Current for an n-CdS Electrode.

Fig. 21. Effect of the Increase in $[\text{Fe}^{2+}]$ on Corrosion Current of an n-CdS Electrode.

were observed, except that there was no break in the curve due to the addition of EDTA. These results indicate that 1) the hole consumption is limited by the mass transport of the reductant molecules in solution, 2) the redox potential of the reductant in solution plays an important role in determining the semiconductor electrode stability, and 3) the kinetics of the electron transfer may also be important. Although thermodynamics of the system dictates that the CdS electrode must be oxidized preferentially in the presence of Fe^{2+} , Fe^{2+} is oxidized at higher concentration ($E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.53 \text{ V vs. SCE}$). This may be possible because the rate of electron transfer would be faster from Fe^{2+} to the valence band than from CdS to its valence band. When EDTA is added, a corresponding amount of the iron(II)-EDTA complex is produced, lowering the redox potential of the reductant to -0.05 V vs. SCE .

To justify the above argument about the kinetics, we determined the rate of heterogeneous electron transfer (k°) at the gold electrode for $\text{Fe}^{3+}/\text{Fe}^{2+}$, iron(III)-EDTA/iron(II)-EDTA, and S/S^{2-} pairs. The constants were determined by the Tafel method²⁷ from the current-voltage curves at a rotating gold electrode. The rate constants were 2.7×10^{-3} , 1.4×10^{-2} , and $4.7 \times 10^{-5} \text{ cm/sec}$, respectively, for above redox pairs. For the S/S^{2-} pair, sodium sulfide was used instead of cadmium sulfide. It should be pointed out that the energy levels of sulfide may be quite different in the solution and solid phases. The k° value for the $\text{Fe}^{3+}/\text{Fe}^{2+}$ pair at a gold electrode is in excellent agreement with the one reported by Gerisher at the Pt-electrode ($3.1 \times 10^{-3} \text{ cm/sec}$)²⁸.

These results indicate that iron(II)-EDTA is, thermodynamically and kinetically, a better electron donor than both Fe^{2+} and sulfide ion. This may explain why Fe^{2+} is oxidized when the oxidation of CdS is more favorable thermodynamically. The iron(II)-EDTA complex also suppresses the anodic photodissolution of the CdS electrode for both thermodynamic and kinetic reasons. The reason for high

photoanodic dissolution currents, when this complex is used, might be that the intracrystal electron transfer from solid state sulfide ion to the valence band is more efficient than the interphase transfer involving the solution and the electrode surface.

Finally, effects of supporting electrolyte concentrations were studied and the results are shown in Fig. 22. We notice in Fig. 22 that the photoanodic dissolution current decreases with increasing supporting electrolyte concentration until it passes a minimum value, after which the dissolution current goes back up. The same trend was observed when the concentration of iron(II)-EDTA or Fe^{2+} was increased. We attribute this to an adsorption effect of the anions, i.e., sulfate and/or chloride ions at the electrode surface. With the n-type semiconductor electrode illuminated, the surface will be positively charged. Thus, anions would be adsorbed at the electrode surface. When the concentration of the supporting electrolyte is low, the increase in its concentration may suppress the photoanodic dissolution process by enhancing the electron transfer with improved solution conductance. But this trend may reverse when the supporting electrolyte concentration becomes high enough to allow a significant amount of adsorbed anions at the surface, hindering the approach of the electron donor molecules. The other evidence for this mechanism is that the minimum photodissolution currents are observed at a concentration of about 0.03 M for $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ (not shown) and about 0.10 M for KCl. This shows that the adsorption is more effective for the sulfate ion than for the chloride ion, which would be expected from their charges. The adsorption process is not clearly understood and does not appear very strong.

When the concentration of Fe^{2+} at the minimum dissolution current was plotted vs. the ionic strength of the solution at the minimum corrosion current, the curve shown in Fig. 23 was obtained. This plot clearly demonstrates that more Fe^{2+} species are needed to have a minimum photodissolution current at higher ionic strengths of the solution due to heavier adsorption.

Fig. 22. Effect of the Concentration of the Supporting Electrolyte Concentration.

Fig. 23. Plot of $[\text{Fe}^{2+}]$ vs. Ionic Strength at the Point of Minimum Corrosion.

D. Discussion

Of various experimental parameters studied, the incident light intensity, the redox potential and the concentration of a reductant, and the concentration of supporting electrolytes appear to have important effects on the electrode stability of n-CdS. Factors such as wavelengths of incident light and the applied potential at the photoanode played a minor role. We have not studied a potential range wide enough to cover the oxidation or the reduction of the electrode material, but for the range we have studied, no significant effects have been observed.

The effects of the incident light intensity and the reductant concentration on electrode stability are attributed to the kinetic reasons, since these parameters would indirectly attenuate the rate of the electron transfer by controlling the donor or the hole (acceptor) concentrations of the PEC system. The thermodynamics of the system was also shown to be important. A clear example is shown in Fig. 21. The instability of the CdS electrode, when the ferrocyanide ion is used as a source of electrons, is also attributed to the thermodynamic reason, for the formal potential for the ferri-/ferrocyanide pair is higher than the dissolution potential of CdS at lower pHs than 4.

Supporting electrolyte appears to decrease the extent of corrosion by improving the conductivity of the solution, thereby improving the electron transfer between two phases at its low concentration. Further increases, however, result in the adsorption of a counter anion, hindering the approach of electron donor molecules toward the electrode.

E. Conclusion

Results shown in this report indicate that the stability of semiconductor electrodes that will be used for photoassisted coal gasification reactions can be studied using rotating ring-disk electrode methods. The semiconductor material should have the valence band energy level more positive than the standard electrode potential for the Fe^{2+} - Fe^{3+} pair. Continued studies need to be carried out for materials having proper conditions for photoassisted electrolysis of coal.

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