

AD-A071 580

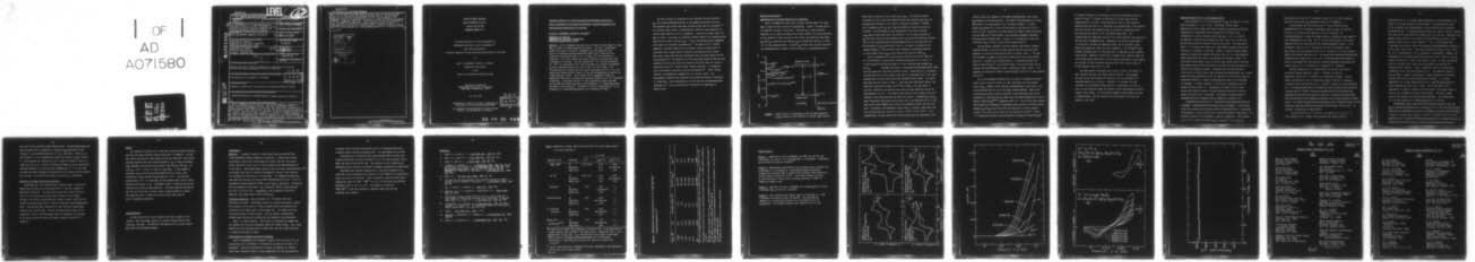
MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMISTRY F/G 7/4
FLAT-BAND POTENTIAL OF N-TYPE SEMICONDUCTING MOLYBDENUM DISULFIDE--ETC(U)
JUL 79 L F SCHNEEMEYER, M S WRIGHTON N00014-78-C-0630

UNCLASSIFIED

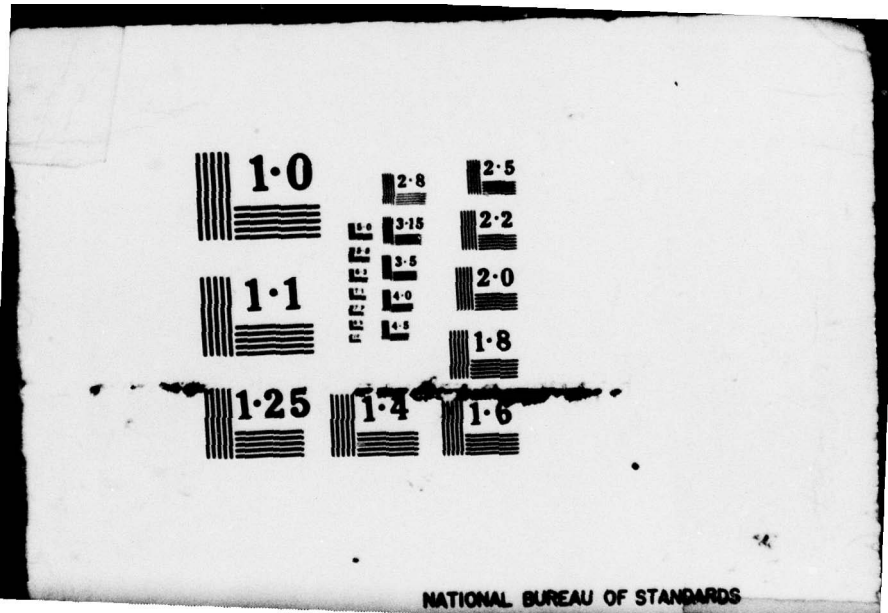
TR-1

NL

| OF |
AD
A071580



END
DATE
FILMED
8-79
DDC



NATIONAL BUREAU OF STANDARDS

UNCLASSIFIED

LEVEL III

BS 12

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

14 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING
1. REPORT NUMBER ONR-TR-1	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER 9
4. TITLE (and Subtitle) Flat-Band Potential of n-Type Semiconducting Molybdenum Disulfide by Cyclic Voltammetry of Two-Electron Reductants: Interface Energetics and the Sustained Photooxidation of Chloride,		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
7. AUTHOR Lynn F. Schneemeyer and Mark S. Wrighton		8. CONTRACT OR GRANT NUMBER(s) 15 N00014-78-C-0630
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 057-696
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE July 18 1979
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 27p.		13. NUMBER OF PAGES 27
		18. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; reproduction is permitted for any purpose of the United States government; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Distribution of this document is unlimited.		
18. SUPPLEMENTARY NOTES Prepared for publication in the Journal of the American Chemical Society		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) photoelectrochemistry, flat-band potential, energy conversion, durability		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Cyclic voltammetry has been used to locate the band edges of n-type MoS ₂ in CH ₃ CN/ and EtOH/[n-Bu ₄ N]ClO ₄ solutions. The crucial experiments concern the study of the cyclic voltammetry of biferrocene (BF) and N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) each of which has two, reversible, one-electron waves at Pt. At MoS ₂ , the first oxidation is reversible in the dark, whereas the second oxidation is observed only upon illumination of the MoS ₂ . The dark oxidation BF → BF ⁺ and the photoanodic BF ⁺ → BF ²⁺ are separated by only ~150 mV allowing us to assign an uncommonly accurate flat-band potential of +0.30 + 0.05 V vs. SCE to		

AD A 071 580

DDC FILE COPY

DDC RECEIVED JUL 24 1979

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE S/N 0102-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

yields

220007

app... VB

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

MoS₂. This accurate flat-band potential reveals that the valence band edge is at ≈ 1.9 V vs. SCE showing that photooxidations doable at TiO₂ are thermodynamically possible at illuminated MoS₂ as well. As an example of the ruggedness of MoS₂ we demonstrate the ability to effect the sustained oxidation of Cl⁻ at illuminated n-type MoS₂. Conclusions from BF are fully supported by those from TMPD and one-electron systems ferrocene, acetylferrocene, 1,1'-diacetylferrocene, and [Ru(2,2'-bipyridine)₃]²⁺. Oxidation of [Ru(2,2'-bipyridine)₃]²⁺ can be effected >0.5 V contrathermodynamically by illumination of MoS₂.

approx.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
LDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Dist.	Avail and/or special
A	

OFFICE OF NAVAL RESEARCH

Contract N00014-78-C-0630

Task No. NR 051-696

TECHNICAL REPORT NO. 1

Flat-Band Potential of n-Type Semiconducting
Molybdenum Disulfide by Cyclic Voltammetry of
Two-Electron Reductants:

Interface Energetics and the Sustained Photooxidation of Chloride

by

Lynn F. Schneemeyer and Mark S. Wrighton

Prepared for Publication

in the

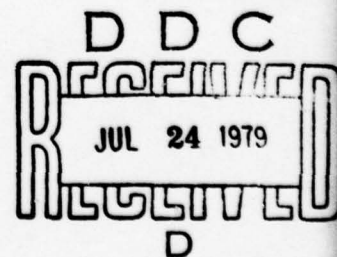
Journal of the American Chemical Society

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

July 18, 1979

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited



79 07 23 049

Flat-Band Potential of n-Type Semiconducting Molybdenum Disulfide by
Cyclic Voltammetry of Two-Electron Reductants: Interface Energetics and
the Sustained Photooxidation of Chloride

by Lynn F. Schneemeyer and Mark S. Wrighton*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

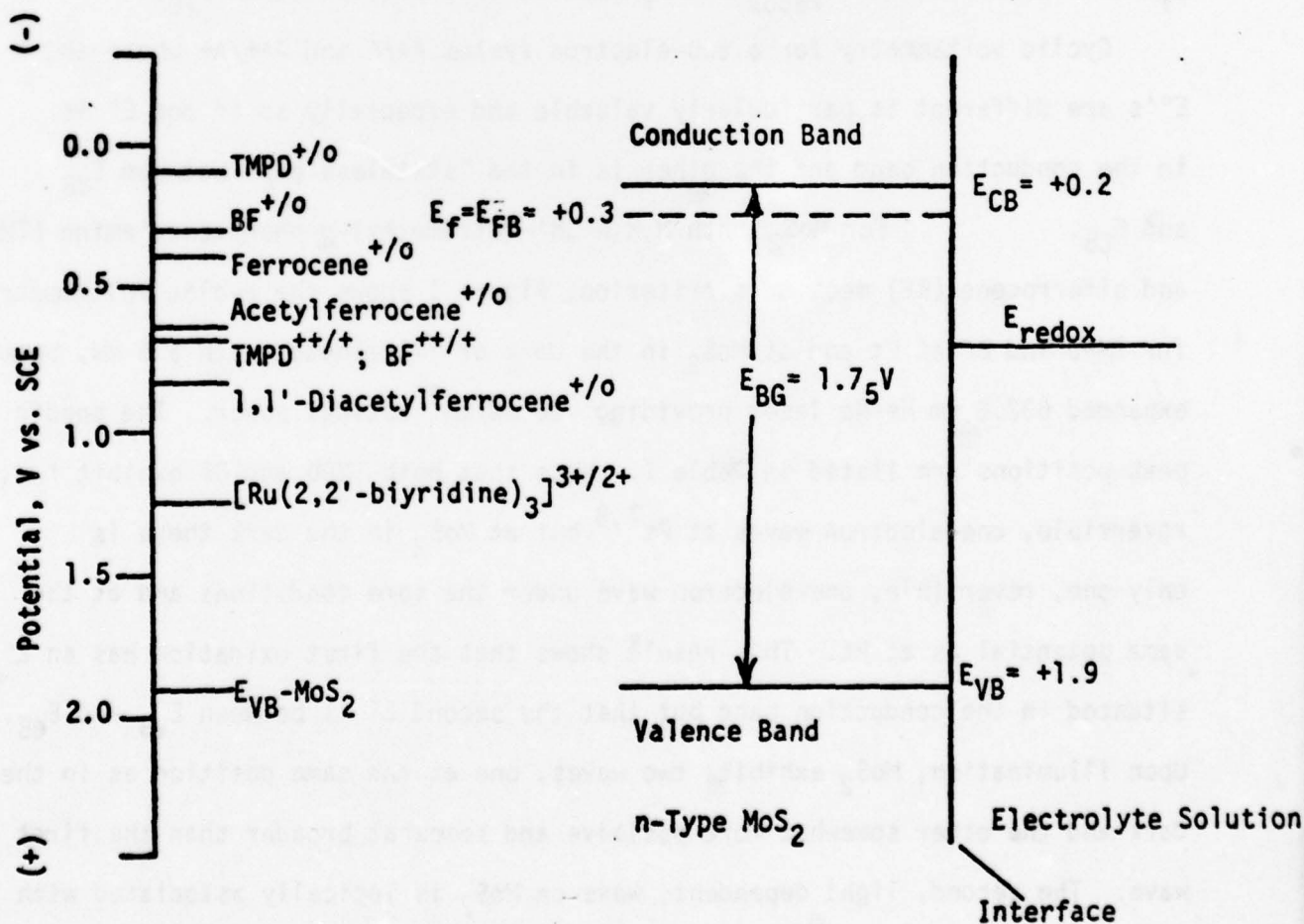
Abstract: Cyclic voltammetry has been used to locate the band edges of n-type MoS_2 in $\text{CH}_3\text{CN}/$ and $\text{EtOH}/[\text{n-Bu}_4\text{N}]\text{ClO}_4$ solutions. The crucial experiments concern the study of the cyclic voltammetry of biferrocene (BF) and N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) each of which has two, reversible, one-electron waves at Pt. At MoS_2 , the first oxidation is reversible in the dark, whereas the second oxidation is observed only upon illumination of the MoS_2 . The dark oxidation $\text{BF} \rightarrow \text{BF}^+$ and the photoanodic $\text{BF}^+ \rightarrow \text{BF}^{++}$ are separated by only ~150 mV allowing us to assign an uncommonly accurate flat-band potential of $+0.30 \pm 0.05$ V vs. SCE to MoS_2 . This flat-band potential reveals that the valence band edge is at ~+1.9 V vs. SCE showing that photooxidations doable at TiO_2 are thermodynamically possible at illuminated MoS_2 as well. As an example of the ruggedness of MoS_2 we demonstrate the ability to effect the sustained oxidation of Cl^- at illuminated n-type MoS_2 . Conclusions from BF are fully supported by those from TMPD and one-electron systems ferrocene, acetylferrocene, 1,1'-diacetylferrocene, and $[\text{Ru}(2,2'\text{-bipyridine})_3]^{2+}$. Oxidation of $[\text{Ru}(2,2'\text{-bipyridine})_3]^{2+}$ can be effected >0.5 V contrathermodynamically by illumination of MoS_2 .

We wish to report an exceptionally well-defined flat-band potential, E_{FB} , for n-type semiconducting MoS_2 in non-aqueous electrolyte solution. The procedure used follows from that outlined by Bard and his co-workers¹⁻³ for locating energy levels of semiconductors relative to the potentials of various redox couples by cyclic voltammetry. Locating the energy levels for MoS_2 is useful, since MoS_2 has attracted interest recently as a photoelectrode material with a small band gap, $E_{BG} = 1.75$ eV, and having unusual ruggedness with respect to photoanodic decomposition.⁴ The material has a layered geometrical structure leading to an electronic (band) structure which is consistent with a lowest optical absorption associated with Mo d-bands. Most other n-type semiconducting photoanodes that have been studied involve p-band materials.⁵ The durability of the n-type MoS_2 photoelectrode has been associated with the fact that the electronic excitation does not involve a transition having $S^{2-} \rightarrow Mo(IV)$ charge transfer character. In a material such as CdS optical excitation involves considerable $S^{2-} \rightarrow Cd(II)$ charge transfer, and photoanodic decomposition is a typical result. Our measurements establish what reductants can be photooxidized by illumination of n-type MoS_2 . Quite interestingly, we find that the contrathermodynamic oxidation of Cl^- can be sustained by illumination of n-type MoS_2 in CH_3CN solvent.

Results and Discussion

Determination of Flat-Band Potential of n-Type MoS₂.

Cyclic voltammetry has been used to locate the band edges for n-type MoS₂ in CH₃CN or EtOH solutions of [n-Bu₄N]ClO₄. Scheme I includes some of our essential findings in this work. The value E_{FB} is that electrode potential, E_f, at which the bands are not bent, Scheme I,⁶ and the evaluation of this potential allows location of the valence and conduction band edges, E_{VB} and E_{CB}, respectively, by knowing E_{BG} and recognizing that E_{FB} is within 0.1 V of the conduction band. Locating E_{VB} reveals what solution reductants are thermodynamically capable of being oxidized by a photogenerated hole



Scheme I: Energy levels of n-type MoS₂ at the flat-band potential E_f = E_{FB} relative to the positions of various redox couples.

which rises to the top of the valence band (E_{VB}). For solution couples A^+/A where E° falls within the conduction band, more negative than E_{CB} , the electrode should behave as if it were a reversible electrode,¹⁻³ whereas for E° between E_{VB} and E_{CB} the n-type semiconductor should be blocking to oxidation. But irradiation of the semiconductor with light of energy $\geq E_{BG}$ should create holes which can oxidize $A \rightarrow A^+$ for any E_f positive of E_{FB} such that sufficient band bending exists to prevent back electron transfer. Thus, A can be photooxidized contrathermodynamically to an extent equal to the difference in E_{FB} and $E^\circ(A^+/A)$; that is, in Scheme I oxidation of the reduced component of the solution can be effected at electrode potentials, E_f , more negative than E_{redox} but E_f must be more positive than E_{FB} .

Cyclic voltammetry for a two-electron system A^+/A and A^{++}/A^+ where the E° 's are different is particularly valuable and especially so if one E° is in the conduction band and the other is in the "stateless gap" between E_{VB} and E_{CB} . For MoS_2 both N,N,N',N' -tetramethyl-*p*-phenylenediamine (TMPD) and biferrocene (BF) meet this criterion; Figure 1 shows the cyclic voltammetry for TMPD and BF at Pt and at MoS_2 in the dark or illuminated with a 5 mW, beam expanded 632.8 nm He-Ne laser providing $\sim 50 \text{ mW/cm}^2$ optical power. The anodic peak positions are listed in Table I. Note that both TMPD and BF exhibit two, reversible, one-electron waves at Pt^{7,8} but at MoS_2 in the dark there is only one, reversible, one-electron wave under the same conditions and at the same potential as at Pt. This result shows that the first oxidation has an E° situated in the conduction band but that the second E° is between E_{VB} and E_{CB} . Upon illumination, MoS_2 exhibits two waves, one at the same position as in the dark and the other somewhat more positive and somewhat broader than the first wave. The second, light dependent, wave on MoS_2 is logically associated with the contrathermodynamic oxidation of $TMPD^+$ to $TMPD^{++}$ or BF^+ to BF^{++} . Quite interestingly, the dark wave for BF and the second wave are separated by only

-150 mV; within the framework of the model developed above, this places E_{FB} between the two peak positions. The onset of the photocurrent for both TMPD and BF is at approximately +0.3 V as seen in Figure 1. We thus bracket E_{FB} between +0.3 V and +0.5 and assign it the value of +0.30 V + 0.05 V vs. SCE. Essentially the same results are found in EtOH solvent but for both TMPD and BF there appear to be adsorption phenomena associated with the second oxidation wave. Further, it is interesting to note that our value of E_{FB} is close to that given for aqueous media.⁴

The one-electron reductant ferrocene behaves consistently; sluggish oxidation obtains in the dark at MoS_2 , despite the fact that the formal potential is only 80 mV more positive than for BF^+/BF , Table I. The wave for ferrocene is broader and the peak-to-peak separation is much greater than at Pt. Oxidation of acetylferrocene, 1,1'-diacetylferrocene, and $[Ru(2,2'\text{-bipyridine})_3]^{2+}$ is not found at MoS_2 in the dark but each can be oxidized contrathermodynamically upon illumination of MoS_2 , Table I. For example, the oxidation of $[Ru(2,2'\text{-bipyridine})_3]^{2+}$ occurs ~0.5 V more negative than at Pt.

All of the reductants examined thus far exhibit a photoanodic current onset in the vicinity of +0.30 V vs. SCE, consistent with the assigned value of E_{FB} . However, we do find that the photoanodic current peak is not at the same position for all of the redox couples employed. Some of the variations may be due to minor variations in the electrodes used, but an explanation is required for the rather large difference between the +0.83 for $[Ru(2,2'\text{-bipyridine})_3]^{3+/2+}$ compared to the +0.5 - +0.6 for the other couples. We attribute the differences in photoanodic peak positions to surface states between E_{VB} and E_{CB} which facilitate the reduction of solution species. Evidence for surface states comes from the observation that BF^{++} , $TMPD^{++}$, 1,1'-diacetylferricenium, acetylferricenium, and $[Ru(2,2'\text{-bipyridine})_3]^{3+}$

all undergo reduction at n-type MoS_2 in the dark at potentials which are positive of E_{FB} .¹⁻³ Crudely, we find that at a given sweep rate the reduction peak in the dark is more positive as the E° of the system in question moves more positive. Often when low concentrations of the oxidized form are involved, the reduction peak in the dark at n-type MoS_2 occurs near the position found at Pt at ~ 100 mV/sec sweep rates. Low concentrations are important since only low current densities are required to see the cyclic voltammetric wave. Apparently, the surface state density is sufficiently low that the reduction current can be overcome at even modest hole generation rates (low light intensity). The ~ 50 mW/cm² light intensity employed here is of the same order of magnitude as that expected from sunlight. Generally, we find that increased light intensity makes the cyclic waves sharper and results in more negative photoanodic current peaks, but the peak is never found more negative than +0.45 V and the onset is no more negative than +0.30 V vs. SCE.

The redox couples investigated and listed in Table I are chosen, in part, because they have fast charge transfer kinetics. But a priori we really do not know whether the kinetics will be as favorable at an electrode material such as MoS_2 . Therefore it is possible that the variation in the photoanodic peak position is attributable, at least in part, to the differences among the couples in their heterogeneous electron transfer rate at MoS_2 . The relationship between surface states, the rate of photooxidation, and dark reduction, and the nature of the solution species is not clear.

Sustained Oxidation of Cl^- in Non-Aqueous Media.

With a band gap of 1.75 eV, the position of E_{VB} for MoS_2 is at a very positive potential, ~ 1.9 V vs. SCE. Accordingly, visible light generation of holes in MoS_2 could lead to oxidation processes as difficult energetically as those which can be effected by ultraviolet light illumination of the very durable n-type TiO_2 ($E_{\text{VB}} \approx + 2.0$ V vs. SCE).⁹ One question is whether such processes do occur, and if so, for how long and with what electrical energy savings by using light. From the data in Table I it is obvious that there are a large number of species that can be oxidized at illuminated, n-type MoS_2 . However, a number of these systems cannot be oxidized with constant efficiency; that is, at a fixed potential where photocurrent does obtain, the photocurrent declines in time. The difficulties would appear to arise from the redox couples used in that the MoS_2 becomes covered with precipitates from either the starting material or from the electrochemical product. Refreshing the electrode surface by rinsing with a suitable solvent does rejuvenate the photocurrent, but it would appear that MoS_2 photoanodes suffer the same sorts of difficulties that are encountered generally in organic electrochemistry where solid electrodes are employed. In these instances it is difficult to determine just how durable the MoS_2 actually is. Accordingly, we sought to find a redox system which could be studied in CH_3CN electrolyte solution in order to assess the durability of n-type MoS_2 . The powerful oxidizing power of photogenerated holes suggested that we attempt the oxidation of Cl^- .

In CH_3CN electrolyte solution Cl^- is susceptible to sustained photooxidation at n-type MoS_2 . Essentially the same findings obtain with LiCl or $[\text{Et}_4\text{N}]\text{Cl}$. Figure 2 shows the equilibrium photocurrent-voltage curves for a solution containing Cl^- . In the $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{n-Bu}_4\text{N}]\text{ClO}_4$ solution no photocurrent is found over the potential range scanned. The oxidation current at a Pt electrode is shown for comparison. The oxidation of Cl^- at Pt is known to produce $\text{Cl}_2/\text{Cl}_3^-$ mixtures.¹⁰ At n-type MoS_2

the photocurrent onset for Cl^- oxidation is near +0.3 V vs. SCE, consistent again with the value of E_{FB} determined from cyclic voltammetry.

It would appear that the oxidation of Cl^- can be effected contra-thermodynamically at illuminated n-type MoS_2 , since the onset of oxidation current is at a more positive potential at the Pt electrode. By "contrathermodynamic" we mean the oxidation occurs at potentials more negative than thermodynamically allowed. But it is the oxidizing power of the photo-generated holes that makes possible the contrathermodynamic process. Cyclic voltammetry, Figure 3, of Cl^- oxidation at Pt and at illuminated n-type MoS_2 reveals that the photoanodic peak for Cl^- oxidation is at a more negative potential than the anodic peak found at Pt. At increased light intensity the photoanodic peak is observed to be as negative as +0.72 V vs. SCE. From the onset potentials for oxidation current it would appear that illumination of an n-type MoS_2 photoanode allows an electrical energy savings of >0.5 V compared to a Pt anode for Cl^- oxidation.

The data summarized for Cl^- photooxidation accord well with that for the various couples detailed in Table I. Moreover, we find the photoanodic current for Cl^- oxidation to be remarkably constant. Figure 4 shows a representative plot of photocurrent against time for Cl^- oxidation. A constant (within 3%) photocurrent of $\sim 1 \text{ mA/cm}^2$ is shown for a period exceeding 10 h. In a subsequent experiment with the same electrode 8h of constant (within 3%) photocurrent was found at $\sim 10 \text{ mA/cm}^2$. Similar experiments have been carried out with other MoS_2 photoelectrodes and the results are essentially invariant. The surface of MoS_2 electrodes used in such media are not visibly changed, and the photocurrent-voltage properties are constant as well. For a number of MoS_2 electrodes we have passed a significantly larger number of moles of electrons through the interface than the number of moles of MoS_2 initially used. No evidence for destruction of MoS_2 obtains.

The photooxidation of Cl^- results in the generation of $\text{Cl}_2/\text{Cl}_3^-$, as with oxidation at Pt. Several facts establish the product identity.

Photooxidation of Cl^- in the MoS_2 anode compartment of a two compartment cell results in a yellow coloration of the solution. The characteristic smell of Cl_2 is present after photooxidation, and the solution gives a positive starch/iodine test. The anolyte potential moves from $\sim 0.0\text{V}$ to $\sim +0.8\text{V}$ vs. SCE or very close to the value obtained by adding Cl_2 to the solution. Addition of the anolyte product solution to a solution of $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ results in the apparent oxidation to an Ir(III) compound.¹¹ Thus, it would appear that n-type MoS_2 can be used to effect the sustained contrathermodynamic generation of Cl_2 using visible light. Given that the band gap of MoS_2 is only 1.75 eV, the $\sim 0.5\text{V}$ "underpotential" for Cl_2 production is respectable. However, the rectangularity of the photocurrent-voltage curves is poor, Figure 2, and the overall efficiency of a light driven process is small. Further, the quantum yield for electron flow is small, and the quantum yield declines with increasing light intensity. Table II summarizes some of the quantitative information culled from an electrochemical cell. The important finding is that the MoS_2 is rugged; an $\text{CH}_3\text{CN}/\text{Cl}_2/\text{Cl}^-$ system comprises an electrolyte solution which yields a stable photocurrent from MoS_2 . In a single compartment cell we have demonstrated that an n-type MoS_2 -based photocell can be operated using the Cl_2/Cl^- couple. On the time scale of our experiments, we found no evidence for chlorination of the organic matter in the cell, but ultimately such would likely obtain. The Cl_2/Cl^- couple would be too corrosive for long duration experiments. But interestingly, it is not the stability of illuminated MoS_2 which is limiting.

The durability of MoS_2 is especially interesting when contrasted to n-type CdS ($E_{\text{BG}} = 2.4\text{ eV}$) which has been established to have $E_{\text{VB}} \sim +1.5\text{ V}$ vs. SCE.² We find that CdS shows substantial anodic decomposition current when illuminated in electrolyte solutions where MoS_2 is stable. In one experiment, for example, n-type CdS illuminated at -0.65 V vs. SCE in the presence of Cl_2/Cl^- such that 2×10^{-5} moles of electrons passed at $\sim 30\text{ mA}/\text{cm}^2$ yields obvious electrode deterioration while MoS_2 illuminated at $+0.8\text{V}$ at the same current density to

pass 4×10^{-5} moles of electrons showed no deterioration. Though CdS has energetics which would indicate that Cl_2 generation is possible (E_{VB} more positive than $E^\circ(\text{Cl}_2/\text{Cl}^-)$), the sustained generation of Cl_2 is not found. Either Cl_2 is never formed or it (or intermediates) attack the surface of CdS to oxidize it. The CdS-based cell employing an I_3^-/I^- couple is durable,¹² but it is likely that the I_3^-/I^- is about as oxidizing a medium as can be tolerated by CdS-based energetics for the CdS anodic decomposition.¹³ It is not clear just what the anodic decomposition energetics are for MoS_2 , since the products are not known. But the ability of MoS_2 to survive Cl_2 is remarkable.

Comparison to Aqueous Electrolyte Solutions.

n-Type MoS_2 was first characterized in aqueous media; in particular photocurrent-voltage curves and photocurrent vs. time was recorded in $\text{H}_2\text{O}/0.1\text{M}$ KCl solutions. The photocurrent onset was in the vicinity of +0.3 V vs. SCE consistent with E_{FB} close to what we find in CH_3CN . Curiously, the earlier characterization of MoS_2 in $\text{H}_2\text{O}/0.1\text{M}$ KCl did not include the consideration that Cl^- could be oxidized by the photogenerated holes. Such may have been responsible for the relatively stable photocurrents found from the MoS_2 . The main finding from our study in this connection is that in the non-aqueous media the energetics are the same as for the H_2O solvent and we do find good, constant current for Cl^- oxidation.

Summary

The interfacial energetics for n-type MoS₂ contacting CH₃CN electrolyte solutions have been accurately defined using cyclic voltammetry. The best data concern two-electron redox couples having one reversible, one-electron wave more negative than the flat-band potential, E_{FB}, of MoS₂ and another, light dependent, one-electron wave having E° more positive than E_{FB}. We find E_{FB} = +0.30 + 0.05 V vs. SCE for n-type MoS₂. A large number of reductants can be oxidized contrathermodynamically by visible light irradiation of MoS₂; maximum photovoltages are ~0.5 V. The sustained photooxidation of Cl⁻ at n-type MoS₂ has been demonstrated; optical energy conversion efficiency is low. Improvement hinges on improving the quantum yield and the current-voltage properties. The poor properties encountered thus far are likely due to surface states situated between the valence and conduction band. Evidence for surface states comes from the cyclic voltammetry experiments.

Acknowledgements

We thank the Office of Naval Research for partial support of this research. MSW acknowledges support as a Dreyfus Teacher-Scholar Grant recipient, 1975-1980. We appreciate the generous gift of single crystal MoS₂ from Climax Molybdenum Company.

Experimental

Materials. A sample of natural, single-crystal MoS_2 was obtained from Climax Molybdenum Company (Greenwich, Connecticut). Samples were cleaved by slipping a sharp steel blade between the layers, then cut into smaller pieces (typically 5 mm x 5 mm x 0.1 mm) by pressing the blade perpendicular to the layers. Spectrograde CH_3CN , absolute EtOH , ferrocene, acetylferrocene, LiCl , and $[\text{Et}_4\text{N}]\text{Cl}$ were used as received from commercial sources, after checking for electroactive impurities at a Pt electrode. 1,1'-Diacetylferrocene does show impurities and was purified by column chromatography prior to use. N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) was purified by sublimation. Biferrocene (BF) was prepared as described in the literature.⁸ $[\text{Ru}(2,2'\text{-bipyridine})_3]^{2+}$ was used as the ClO_4^- salt. $[\text{n-Bu}_4\text{N}]\text{ClO}_4$, from Southwestern Analytical Chemicals, was vacuum dried at 70°C for 24 hours.

Electrode Preparation. MoS_2 electrodes ($\sim 0.1 \text{ cm}^2$ exposed area) were fabricated as follows. Satisfactory electrical contacts were made by rubbing Ga-In eutectic on one side of a freshly cleaved crystal and mounting (with conducting silver epoxy) onto a coiled copper wire. The copper wire lead was passed through 4 mm Pyrex tubing and the assembly insulated with ordinary epoxy leaving only the MoS_2 001 face exposed to the electrolyte.

MoS_2 is a fragile material. The surface is susceptible to damage from too vigorous stirring which presumably shears off flakes of MoS_2 . Also, rough handling can cause the epoxy seal to break loose from the surface resulting in leakage to the metallic mount.

Electrochemical Equipment and General Procedures

Cyclic voltammograms were recorded in CH_3CN or EtOH solutions of 0.1 M $[\text{n-Bu}_4\text{N}]\text{ClO}_4$ using a PAR Model 173 potentiostat equipped with a Model 175 programmer. Scans were recorded with a Houston Instruments X-Y recorder. Except where otherwise stated, a single compartment cell was used employing

a standard three electrode configuration with a Pt counterelectrode and a saturated calomel reference electrode (SCE). All measurements are for 25°C.

Electrodes were illuminated using a beam expanded 632.8 nm He-Ne laser (Coherent Radiation) providing $\sim 50 \text{ mW/cm}^2$ or an Ar ion laser (Spectra Physics Model 164) tuned to the 514 nm line. The intensity of the irradiation was determined using a Tektronix J16 digital radiometer equipped with a J6502 probe.

Electrodes were routinely checked prior to use and re-checked at the completion of most experiments by scanning in a 0.5 M TMPD/0.1 M $[\text{n-Bu}_4\text{N}]\text{ClO}_4/\text{-CH}_3\text{CN}$ electrolyte at 100 mV/sec. Under illumination, good electrodes show a photocurrent onset for $\text{TMPD}^+ \rightarrow \text{TMPD}^{++}$ at $\sim 0.3 \text{ V vs. SCE}$ with a well-defined photoanodic peak at $\sim 0.5 \text{ V vs. SCE}$. The presence of a wave for $\text{TMPD}^+/\text{TMPD}^{++}$ in the dark indicates an imperfect epoxy seal and such electrodes were rejected.

References

1. Frank, S. N.; Bard, A. J. J. Am. Chem. Soc., 1975, 97, 7427.
2. Kohl, P. A.; Bard, A. J. J. Am. Chem. Soc., 1977, 99, 7531.
3. Laser, D.; Bard, A. J. J. Phys. Chem., 1976, 80, 459.
4. Tributsch, H.; Bennett, J. C. J. Electroanal. Chem., 1977, 81, 91; for related work see Tributsch, H. J. Electrochem. Soc., 1978, 125, 1086; Ber. Bunsenges. Phys. Chem., 1977, 81, 361 and 1978, 82, 169 and Gobrecht, J.; Tributsch, H.; Gerischer, H. J. Electrochem. Soc., 1978, 125, 2085.
5. Nozik, A. J. Ann. Rev. Phys. Chem., 1978, 29, 189.
6. The model for the semiconductor/liquid junction detailed in Scheme I follows from the treatment in Gerischer, H. J. Electroanal. Chem., 1975, 58, 263.
7. Yao, T.; Musha, S.; Munemori, M. Chem. Lett., 1974, 939.
8. Morrison, Jr. W. H.; Krogsrud, S.; Hendrickson, D. N. Inorg. Chem., 1973, 12, 1998.
9. The position of E_{yg} in CH_3CN solution +2.0 V vs. SCE is from ref. 1 and a number of interesting oxidations can be effected by illuminated TiO_2 : Frank, S. N.; Bard, A. J. J. Am. Chem. Soc., 1977, 99, 4667.
10. (a) Kolthoff, I.M.; Coetsee, J.F. J. Am. Chem. Soc., 1957, 79, 1852; (b) Mann, C.K.; Barnes, K.K. "Electrochemical Reactions in Non-Aqueous Media", Marcel Dekker, Inc.: New York, 1970.
11. Vaska, L. Accs. Chem. Res., 1968, 1, 335.
12. Nakatani, K.; Matsudaira, S.; Tsubomura, H. J. Electrochem. Soc., 1978, 125, 406.
13. Bard, A. J.; Wrighton, M. S. J. Electrochem. Soc., 1977, 124, 1706.

Table I. Comparison of Anodic Peak Current Positions for Various Redox Couples at Pt and n-Type MoS₂.^a

Reductant; A, A ⁺	Electrode	V vs. SCE		
		E ^o ^b	E _{PA} (A ⁺ /A)	E _{PA} (A ²⁺ /A ⁺)
TMPD, TMPD ⁺	Pt	0.10, 0.68	0.14	0.82
	MoS ₂ (dark)		0.15	Not Observed
	MoS ₂ (light)		0.15	0.58
BF, BF ⁺	Pt	0.30, 0.67	0.34	-0.67
	MoS ₂ (dark)		0.34	Not Observed
	MoS ₂ (light)		0.34	0.50
Ferrocene	Pt	0.38	0.42	----
	MoS ₂ (dark)		0.50(broad) ^c	----
	MoS ₂ (light)		0.48	----
Acetylferrocene	Pt	0.63	0.66	----
	MoS ₂ (dark)		Not Observed	----
	MoS ₂ (light)		0.54	----
1,1'-Diacetylferrocene	Pt	0.83	0.87	----
	MoS ₂ (dark)		Not Observed	----
	MoS ₂ (light)		0.59	----
[Ru(2,2'-bi-pyridine) ₃] ^{3+/2+}	Pt	1.25	1.30	----
	MoS ₂ (dark)		Not Observed	----
	MoS ₂ (light)		0.83	----

^aAll data are for CH₃CN/0.1M [n-Bu₄N]ClO₄ solutions at 20°. Pt and MoS₂ data for a given reductant were recorded in the same solution. Reductants are at ~1 mM concentration in each case. E_{PA} is the position of the anodic current peak; TMPD is N,N,N',N'-tetramethyl-p-phenylenediamine; BF is biferrocene. Illumination of n-type MoS₂ was with 632.8 nm light from a He-Ne laser (50 mW/cm²).

^bThese E^o's are from cyclic voltammetry at Pt-foil electrodes in the electrolyte solution used for all other studies.

^cSee text.

Table II. Representative Output Characteristics for an n-Type MoS₂-Based Photoelectrochemical Cell.^a

Input, mW ^b	ϕ_e^c	Max power output, μW^b	Max V(V @ η_{max}^d)	$\eta_{\text{max}}, \%e$
0.660	0.20	3.40	400 (170)	0.52
2.90	0.13	7.20	400 (120)	0.24
8.62	0.074	12.6	440 (120)	0.15
27.0	0.038	22.8	470 (120)	0.084
80.9	0.017	33.1	510 (120)	0.041
183	0.009	43.7	530 (140)	0.024

^aAll data for CH₃CN/0.1M [n-Bu₄N]ClO₄/0.2M [Et₄N]Cl with Cl₂ added to bring E_{redox} to +0.82 V vs. SCE.

^bInput power is the 514 nm line from a Spectra-Physics Argon-ion laser. For power density, multiply by 56 cm⁻².

^cQuantum yield for electron flow at E_{redox}; this corresponds to the short-circuit quantum yield taken to be the number of electrons passed per incident photon.

^dMaximum voltage is the open-circuit photopotential and the value in parenthesis is the output voltage at the maximum power point.

^eEfficiency for conversion of 514 nm light to electricity.

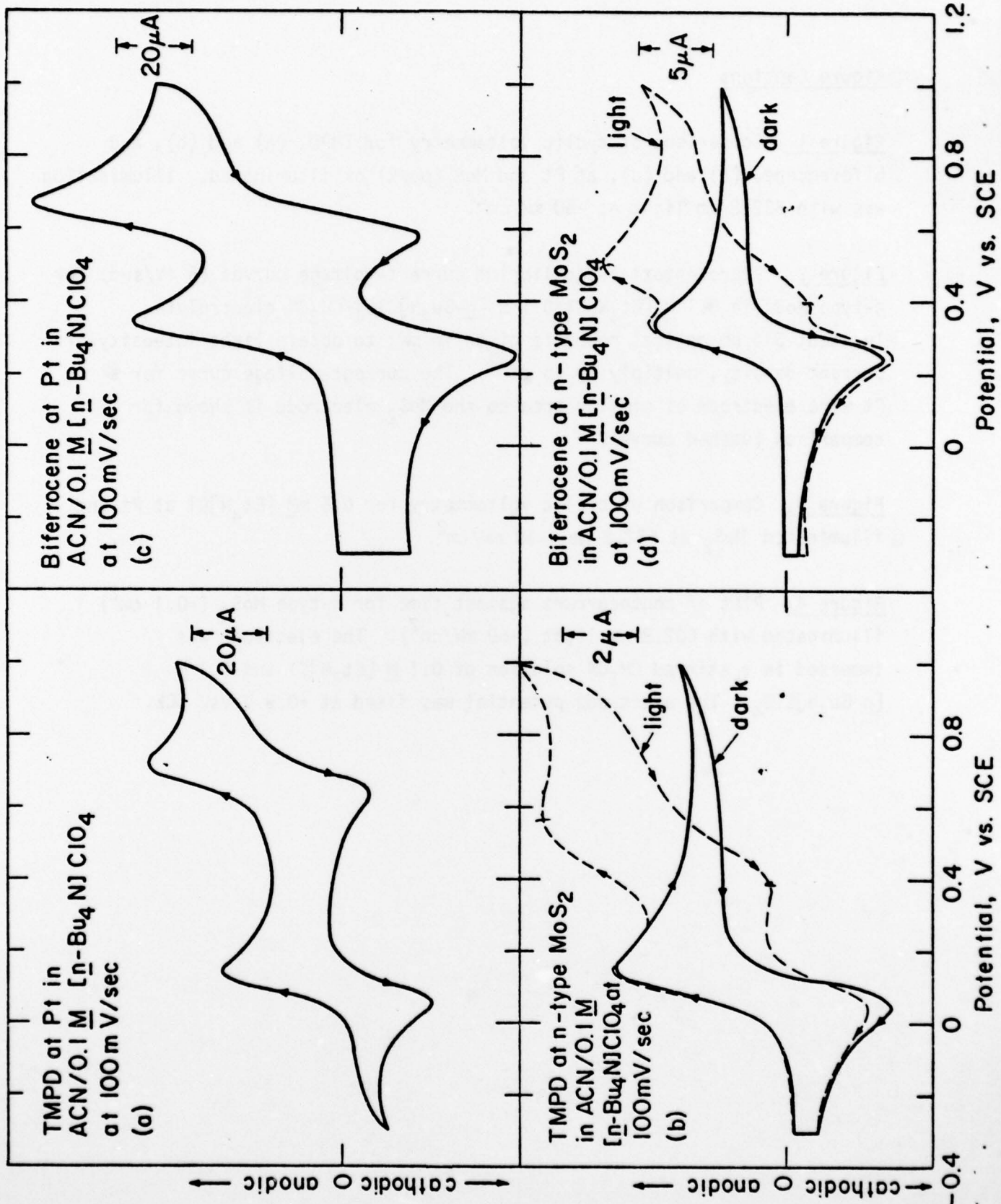
Figure Captions

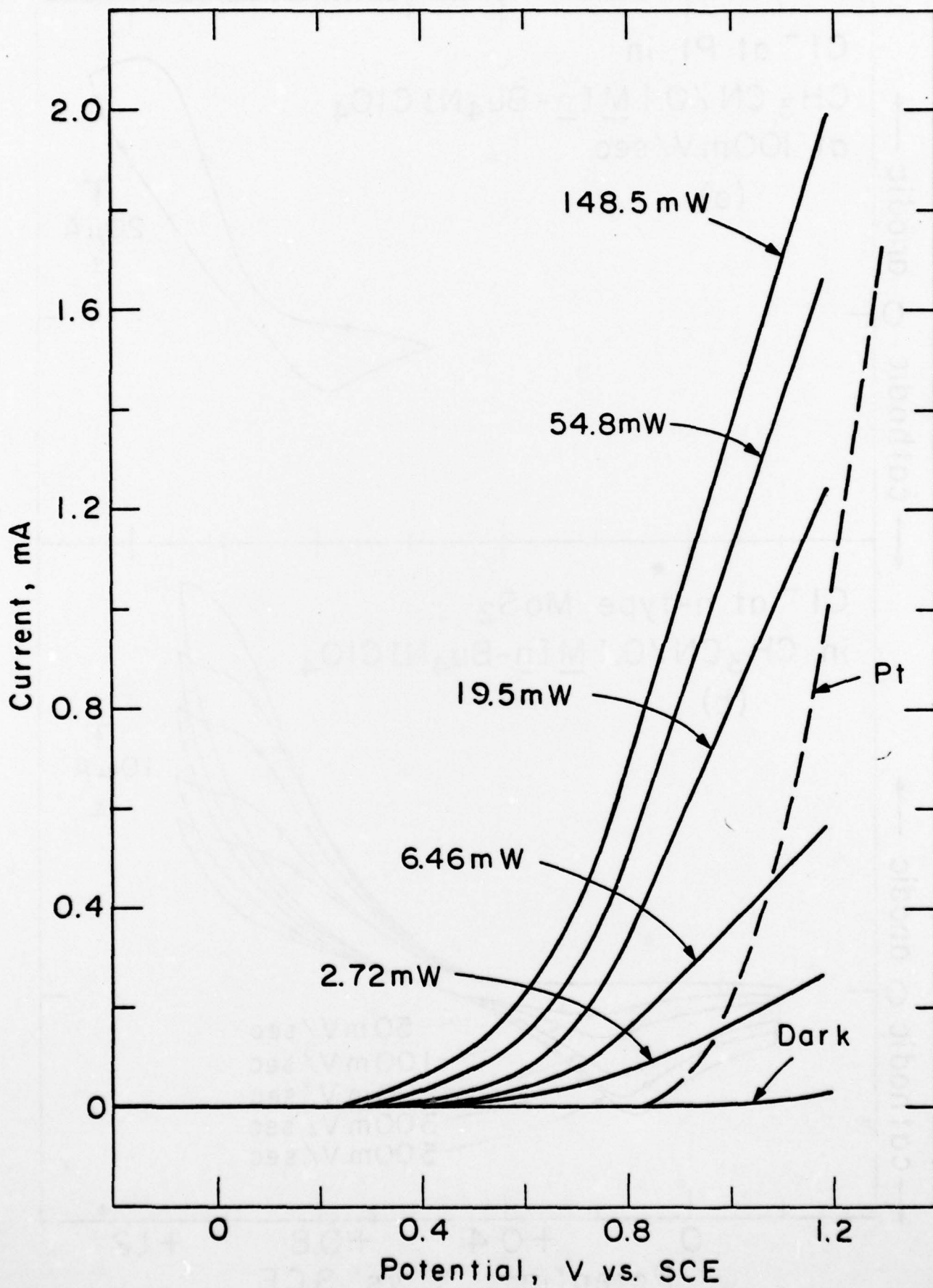
Figure 1. Comparison of cyclic voltammetry for TMPD, (a) and (b), and biferrocene, (c) and (d), at Pt and MoS₂(dark) or illuminated. Illumination was with 632.8 nm light at ~50 mW/cm².

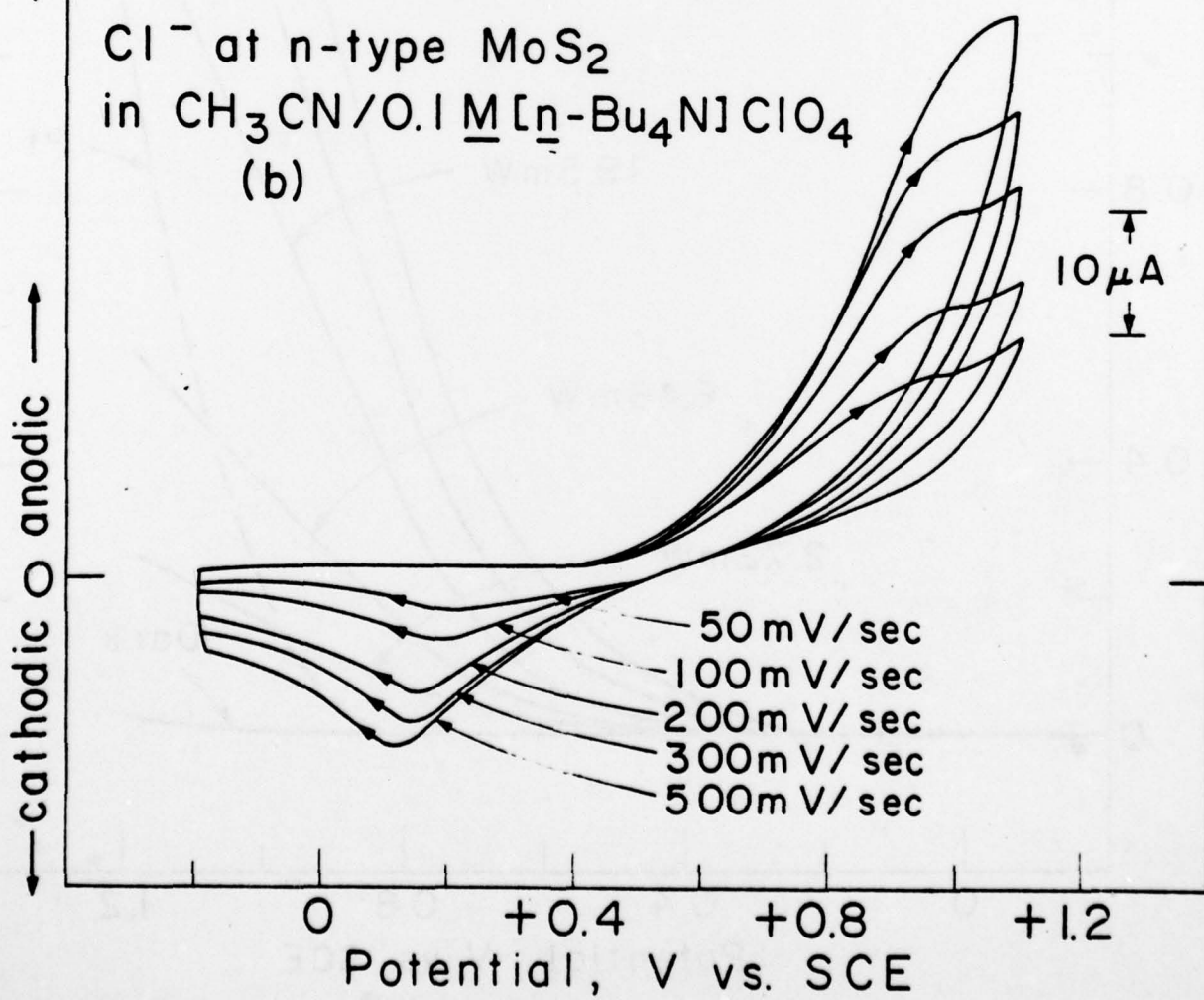
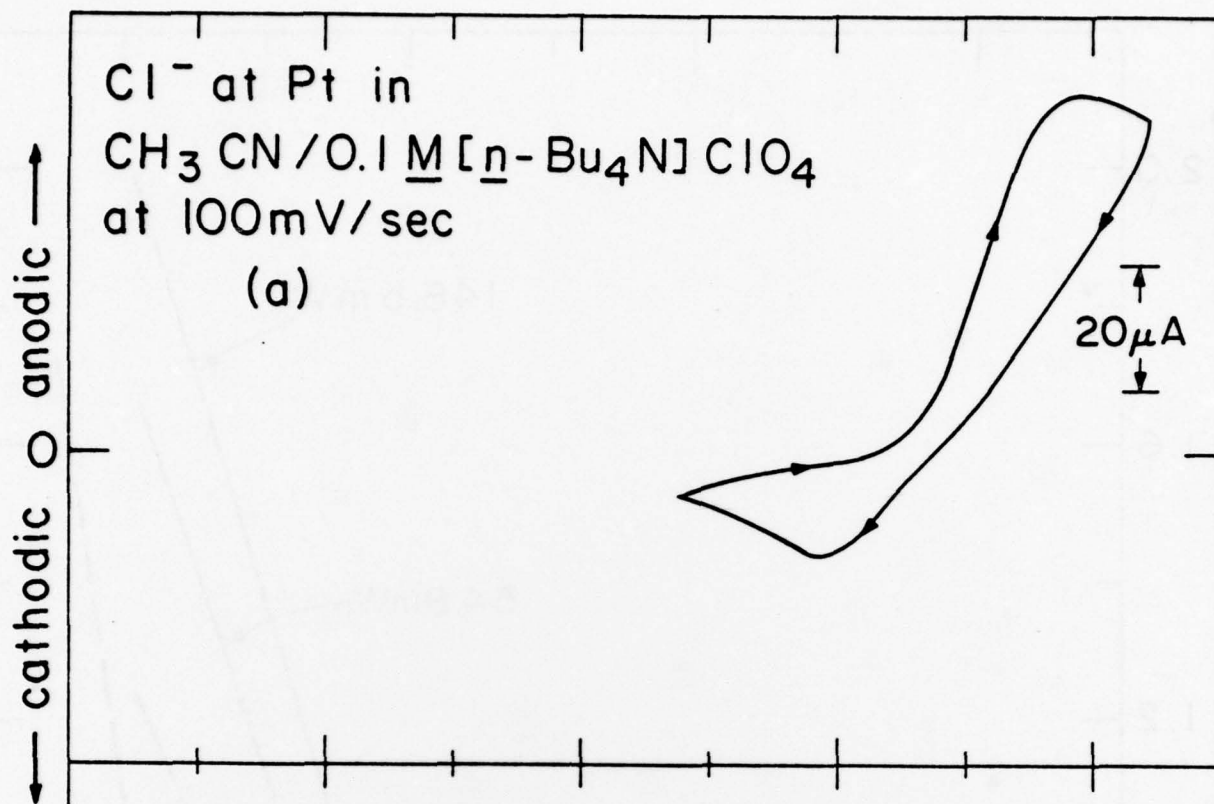
Figure 2. Representative equilibrium current-voltage curves (5 mV/sec) for n-type MoS₂ in 0.1 M [Et₄N]Cl/0.1 M [n-Bu₄N]ClO₄/CH₃CN electrolyte. Incident 514 nm optical power is given in mW; to obtain light intensity or current density, multiply by 15 cm⁻². The current-voltage curve for a Pt wire electrode of similar area to the MoS₂ electrode is shown for comparison (dashed curve).

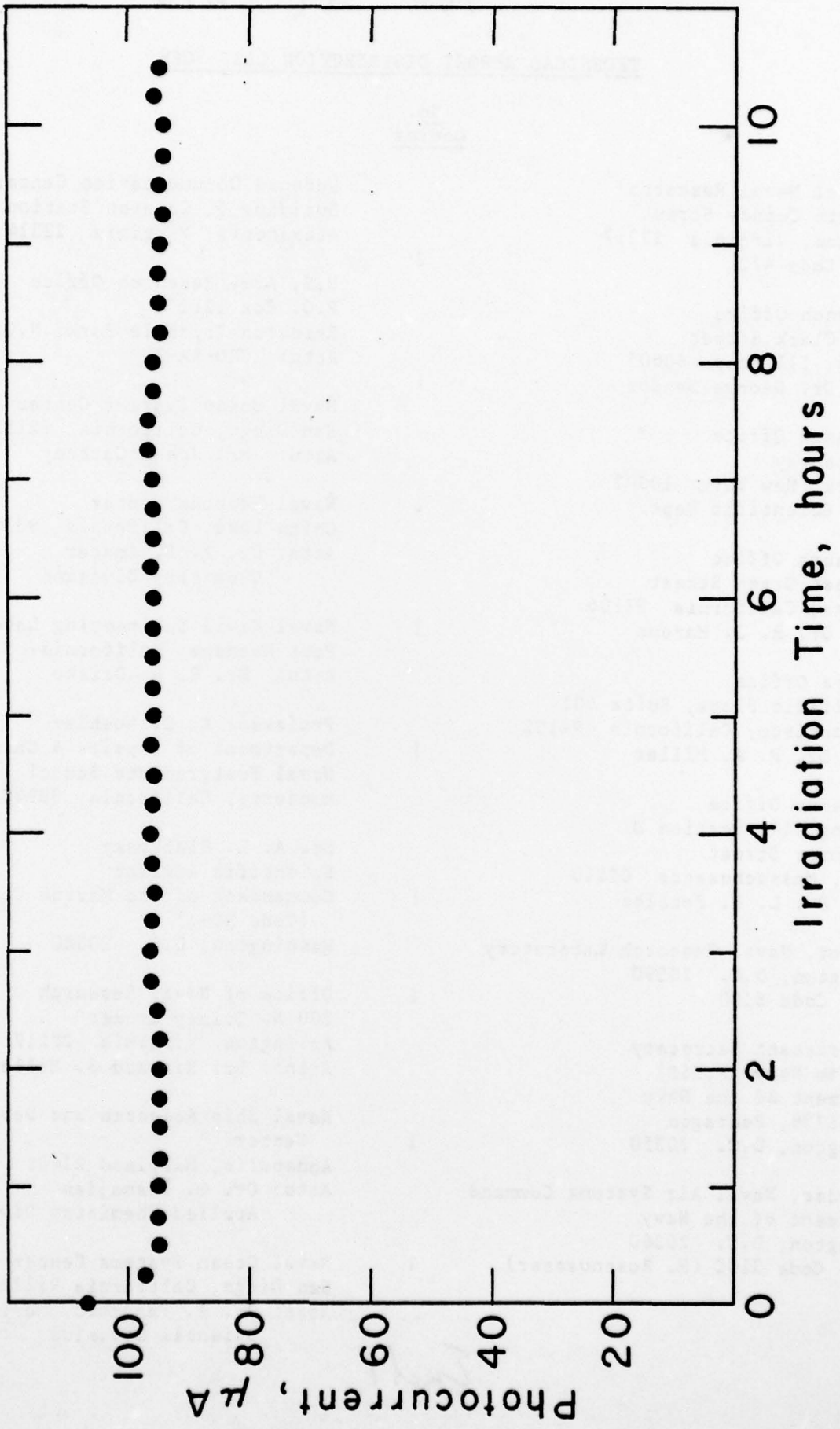
Figure 3. Comparison of cyclic voltammetry for 0.5 mM [Et₄N]Cl at Pt and illuminated MoS₂ at 632.8 nm, ~50 mW/cm².

Figure 4. Plot of photocurrent against time for n-type MoS₂ (~0.1 cm²) illuminated with 632.8 nm light (~50 mW/cm²). The electrode was immersed in a stirred CH₃CN solution of 0.1 M [Et₄N]Cl and 0.1 M [n-Bu₄N]ClO₄. The electrode potential was fixed at +0.9 V vs. SCE.









For 359 - 696

472:GAN:716:tam
78u472-608

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 Attn: Code 472	2	Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. George Sandoz	1	U.S. Army Research Office P.O. Box 1211 Research Triangle Park, N.C. 27709 Attn: CRD-AA-IP	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1	Naval Weapons Center China Lake, California 93555 Attn: Dr. A. B. Amster Chemistry Division	1
ONR Area Office One Hallidie Plaza, Suite 601 San Francisco, California 94102 Attn: Dr. P. A. Miller	1	Naval Civil Engineering Laboratory Port Hueneme, California 93401 Attn: Dr. R. W. Drisko	1
ONR Branch Office Building 114, Section D 666 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1	Professor K. E. Woehler Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Washington, D.C. 20390 Attn: Code 6100	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (R,E&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1	Naval Ship Research and Development Center Annapolis, Maryland 21401 Attn: Dr. G. Bosmajian Applied Chemistry Division	1
		Naval Ocean Systems Center San Diego, California 91232 Attn: Dr. S. Yamamoto, Marine Sciences Division	1

Encl 1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. Paul Delahay New York University Department of Chemistry New York, New York 10003	1	Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1
Dr. R. A. Osteryoung Colorado State University Department of Chemistry Fort Collins, Colorado 80521	1	Dr. P. J. Hendra University of Southampton Department of Chemistry Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Case Western Reserve University Department of Chemistry Cleveland, Ohio 41106	1	Dr. Sam Perone Purdue University Department of Chemistry West Lafayette, Indiana 47907	1
Dr. D. N. Bennion University of California Chemical Engineering Department Los Angeles, California 90024	1	Dr. Royce W. Murray University of North Carolina Department of Chemistry Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus California Institute of Technology Department of Chemistry Pasadena, California 91125	1	Naval Ocean Systems Center San Diego, California 92152 Attn: Technical Library	1
Dr. J. J. Auburn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. J. H. Ambrus The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Telephone Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles & Space Co, Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Oakland University Department of Chemistry Rochester, Michigan 48063	1
Dr. E. Brummer EIC Incorporated Five Lee Street Cambridge, Massachusetts 02139	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>	
Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1	The Reliability Analysis Center RADC (RBRAC) Griffiss AFB, New York 13441
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	
Larry E. Plew Naval Weapons Support Center Code 3073, Building 2906 Crane, Indiana 47522	1	
S. Ruby DOE (STOR) 600 E Street Washington, D.C. 20545	1	
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California 92803	1	
Dr. M. G. Sceats University of Rochester Department of Chemistry Rochester, New York 14627	1	