UNCLASSIFIED

AD NUMBER

AD869155

NEW LIMITATION CHANGE

TO

Approved for public release, distribution unlimited

FROM

Distribution authorized to U.S. Gov't. agencies and their contractors; Critical Technology; APR 1970. Other requests shall be referred to U.S. Army Electronics Command, Attn: AMSEL-KL-PB, Fort Monmouth, NJ 07703-5601.

AUTHORITY

Army Electronics Command ltr dtd 27 Jul 1971

THIS PAGE IS UNCLASSIFIED

# Research and Development Technical Report
ECOM- 0143-3

## ELECTRODE-ELECTROLYTE INTERACTIONS
## MAGNESIUM ANODES : : meta-DINITROBENZENE CATHODES

THIRD SEMI-ANNUAL REPORT

By

A. ADUBIFA

G. SMALDONE

G. STERN

L. WIKSTROM

APRIL, 1970

**DISTRIBUTION STATEMENT**

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of CG, U.S. Army Electronics Command, Fort Monmouth, N. J.
Attn: AMSEL- KL-PB

ECOM
UNITED STATES ARMY ELECTRONICS COMMAND · FORT MONMOUTH, N.J.
CONTRACT DAAB07-68-C-0143
NEW YORK UNIVERSITY
CHEMICAL ENGINEERING DEPARTMENT
Bronx, N. Y.

23

# Electrode - Electrolyte Interactions
# Magnesium Anodes: meta-Dinitrobenzene Cathodes

1 January 1969 to 30 June 1969

Report No. 3

Contract No. DAAB07 - 68-C-0143

Prepared by

A. Adubifa

G. Smaldone

G. Stern

L. Wikstrom

NEW YORK UNIVERSITY

DEPARTMENT OF CHEMICAL ENGINEERING

U. S. ARMY ELECTRONICS COMMAND

FORT MONMOUTH, NEW JERSEY

# Table of Contents

## List of Figures

## Abstract

The electrochemical dissolution of magnesium (AZ-21) and hydrogen evolution reaction on magnesium in $Mg(ClO_4)_2$, $Sr(ClO_4)_2$, $NaClO_4$ and $NaClO_4$ - $Mg(ClO_4)_2$ electrolyte mix have been investigated. The electrochemical reduction of meta-dinitrobenzene in $NaClO_4$ and $Mg(ClO_4)_2$ has also been studied. Polarization data indicate the corrosion current density of the magnesium electrode is much smaller in the $NaClO_4$ than in the other electrolytes studied. In the $NaClO_4$ - $Mg(ClO_4)_2$ electrolyte mix the corrosion current density of the magnesium electrode increases as the proportion of $Mg(ClO_4)_2$ is increased. In the mixed electrolyte system the magnesium electrode can exhibit two distinctly different corrosion current densities. These corrosion current densities are dependent upon the history of the electrode.

The rate of meta-dinitrobenzene reduction in $NaClO_4$ and $Mg(ClO_4)_2$ was found to be about equal. Even though the reduction rate in the two electrolytes was equal, different reaction products apparently were formed.

## Purpose

The purpose of this study is to investigate the electrochemical characteristics of the magnesium anode and the meta-dinitrobenzene cathode in like electrolytes. Much emphasis was paid to the reproducibility of the polarization data.

## Introduction

Previously, the initial results of the investigation of the electrochemical dissolution and corrosion of magnesium and the reduction of meta-dinitrobenzene in aqueous electrolyte were reported(1,2). A review of the pertinent literature was also presented(1). The material presented within this report represents a continuation of the work described earlier(1).

## Experimental Procedure

The electrochemical cell, three electrode system employed, and the experimental procedure followed for the investigation of the magnesium electrodes (AZ-21) were described previously(1). Starting potentials of -1.65v, -1.70v, -1.75v, -1.80v, and -1.85v with potential increments of 25 mv were used in this investigation. The electrolytes used are listed in Table I.

TABLE I

ELECTROLYTES INVESTIGATED

| | |
|---|---|
| 2.0M | $Mg(ClO_4)_2$ |
| 4.0M | $NaClO_4$ |
| 3.96M | $NaClO_4$ - 0.02M $Mg(ClO_4)_2$ |
| 3.60M | $NaClO_4$ - 0.2M $Mg(ClO_4)_2$ |
| 2.80M | $NaClO_4$ - 0.6M $Mg(ClO_4)_2$ |
| 0.5M | $Sr(ClO_4)_2$ |
| 1.0M | $Sr(ClO_4)_2$ |
| 2.0M | $Sr(ClO_4)_2$ |

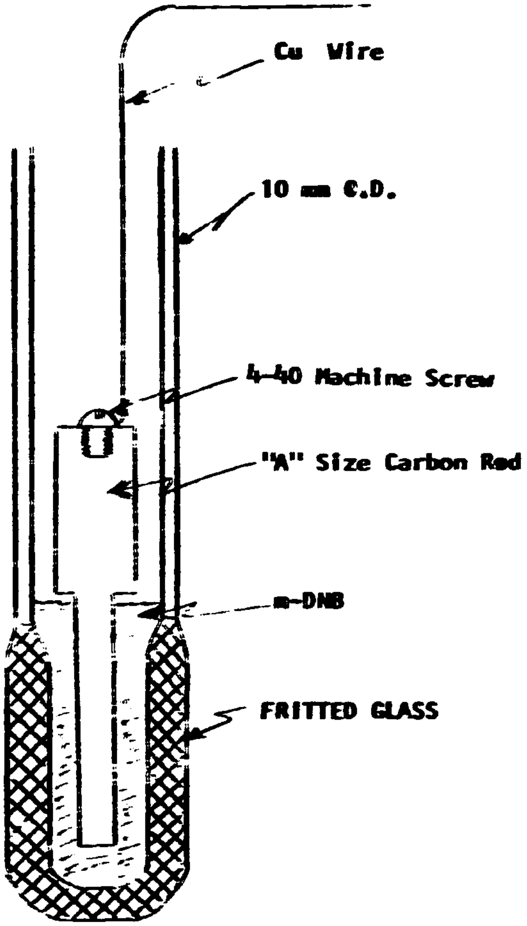
Again, the test electrodes investigated were standard "A" magnesium (AZ-21) cans. A constant surface area was obtained by immersing the open end of each battery can into molten prepurified paraffin wax. As masked, the wax free end of the magnesium can provide a surface area of 14 $cm^2$.

The unmasked end of the magnesium can was immersed into the solution being investigated. The electrode remained at open circuit until a stable rest potential was recorded. The can was then initiated by setting the potential of the magnesium test electrode at the initial value for a duration of 10 minutes. Potential increments of 25 mv were used. At the end of 5 minutes the current was recorded.

The electrochemical reduction of meta-dinitrobenzene in the aqueous perchlorate electrolyte has also been initiated. The test electrode arrangement is shown in Figure 1.

The meta-dinitrobenzene was placed in the 10 mm fritted glass bubbler. A standard "A" size carbon rod, machined to 0.110 inch for the bottom 1.0 inch was used as the cathode. This cathode was attached to a Cu lead with a 4-40 machine screw threaded in the top of the carbon rod. This carbon rod assembly was inserted into the inside of the fritted glass bubbler, in which the meta-dinitrobenzene had been placed, with a plunger. This whole assembly was now immersed in the electrolyte. Sufficient time was allowed for diffusion of electrolyte into the bubbler. The rest potential was allowed to

FIGURE 1 CATHODE ASSEMBLY



stabilize and was then recorded. The taking of the polarization data was then initiated. The following regime was followed:

1. The chosen potential was applied. The current was monitored on the type 564 Memoscope. When a steady-state current was reached, probably not a true steady-state, the current was recorded. Time duration was approximately 3 minutes.

2. The potential was switched back to the rest potential. The current was monitored until no measurable current passed.

3. The potential was switched to the next chosen value - and so-on.

## Results and Discussion

Figure 2 shows the polarization data for magnesium (AZ-21) in aqueous perchlorate electrolyte. These data were taken with a starting potential of -1.80v vs SCE. The closed symbols represent data taken with anodic potential steps and the open symbols represent data taken with cathodic potential steps. From Figure 2 it is seen that as the proportion of $Mg(ClO_4)_2$ in the electrolyte is increased, the hysteresis between the polarization data taken in the anodic and cathodic direction increased. The corrosion current density also increased sharply. With increasing $Mg(ClO_4)_2$ concentration in the electrolyte the magnesium electrode established two, very different, corrosion current densities. These corrosion current densities are,

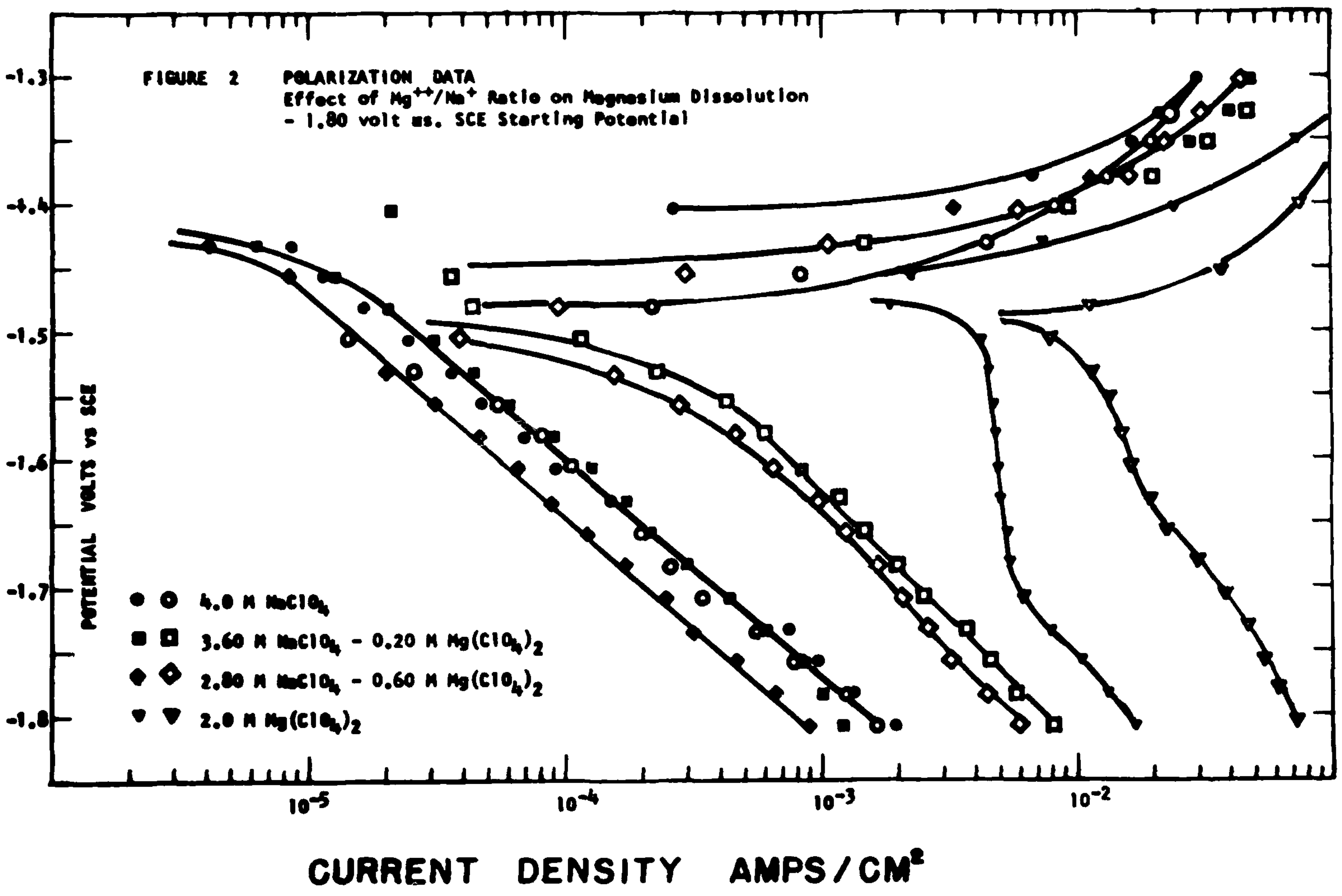


FIGURE 2 POLARIZATION DATA
Effect of $Mg^{++}/Na^{+}$ Ratio on Magnesium Dissolution
- 1.80 volt vs. SCE Starting Potential

as Figure 2 shows, a function of the polarization history of the individual electrode and $Mg(ClO_4)_2$ concentration. Figure 3 shows similar polarization data for magnesium in aqueous perchlorate electrolyte with a starting potential -1.70v vs SCE. These data exhibit the same characteristic as the data with a starting potential of -1.80v vs SCE. From these figures, it is seen that there is a need for polarization data taken in a solution with the composition

1.60M $NaClO_4$
1.20M $Mg(ClO_4)_2$

and/or

0.80M $NaClO_4$
1.60M $Mg(ClO_4)_2$

or possibly a greater proportion of $Mg(ClO_4)_2$.

Figure 4 shows the effect of starting potential with the electrolyte 2.8M $NaClO_4$ - 0.6M $Mg(ClO_4)_2$. These data are remarkably reproducible for a magnesium electrode. This figure also shows that these data are well behaved and predictable. The starting potential does not appear to influence these data.

Figure 5 shows the polarization data for a magnesium (AZ-21) electrode in $Sr(ClO_4)_2$. Concentrations of 4.0M, 2.0M, 1.0M and 0.5M were investigated. The 4.0M $Sr(ClO_4)$ solution was exceedingly viscous. The polarization data indicate that the rest potential and corrosion current densities are a strong function of concentration. In a given $Sr(ClO_4)_2$ electrolyte the magnesium electrode exhibited two apparently

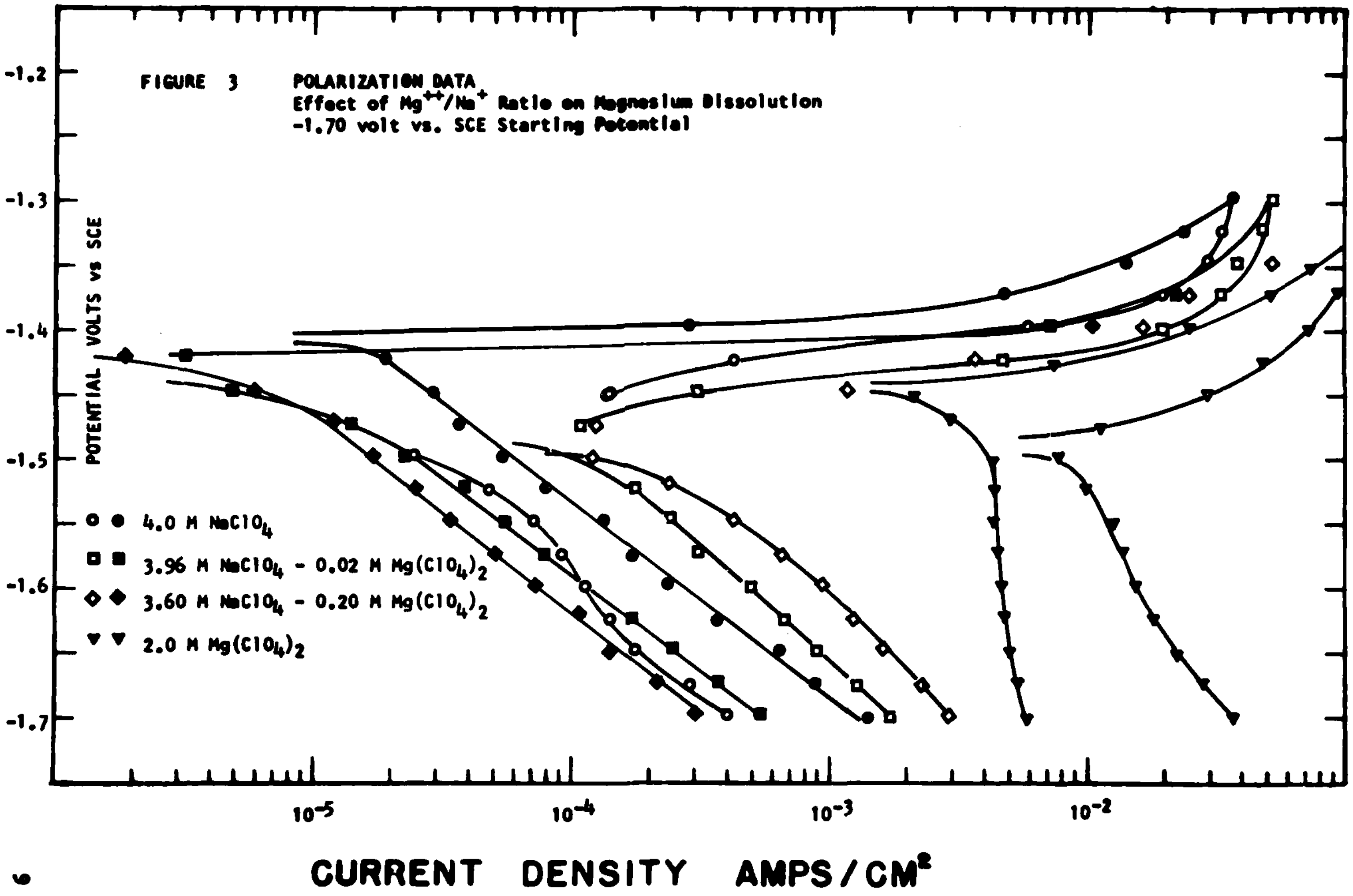


FIGURE 3 POLARIZATION DATA
Effect of $Mg^{++}/Na^{+}$ Ratio on Magnesium Dissolution
-1.70 volt vs. SCE Starting Potential

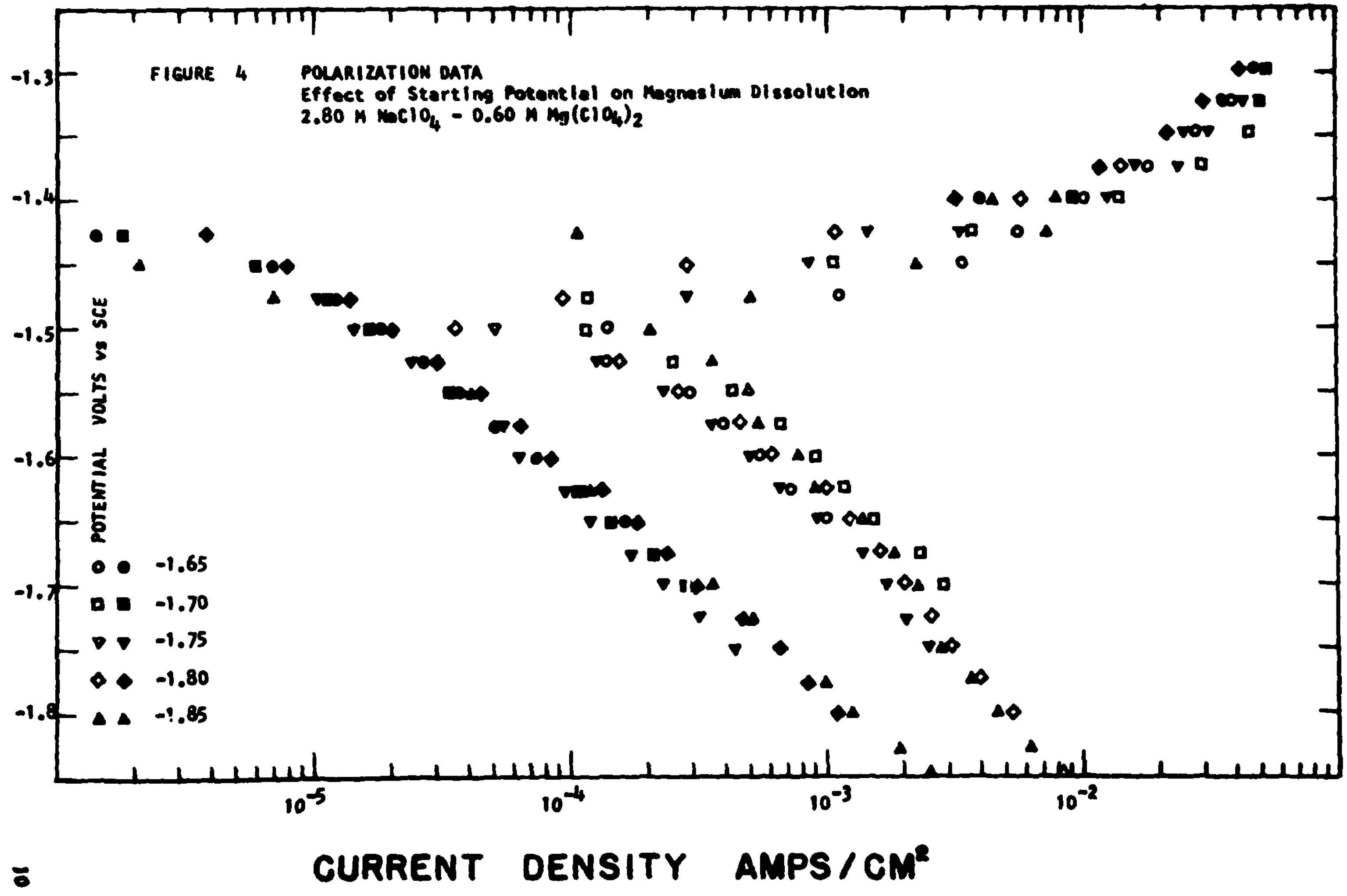


FIGURE 4 POLARIZATION DATA
Effect of Starting Potential on Magnesium Dissolution
2.80 M $NaClO_4$ - 0.60 M $Mg(ClO_4)_2$

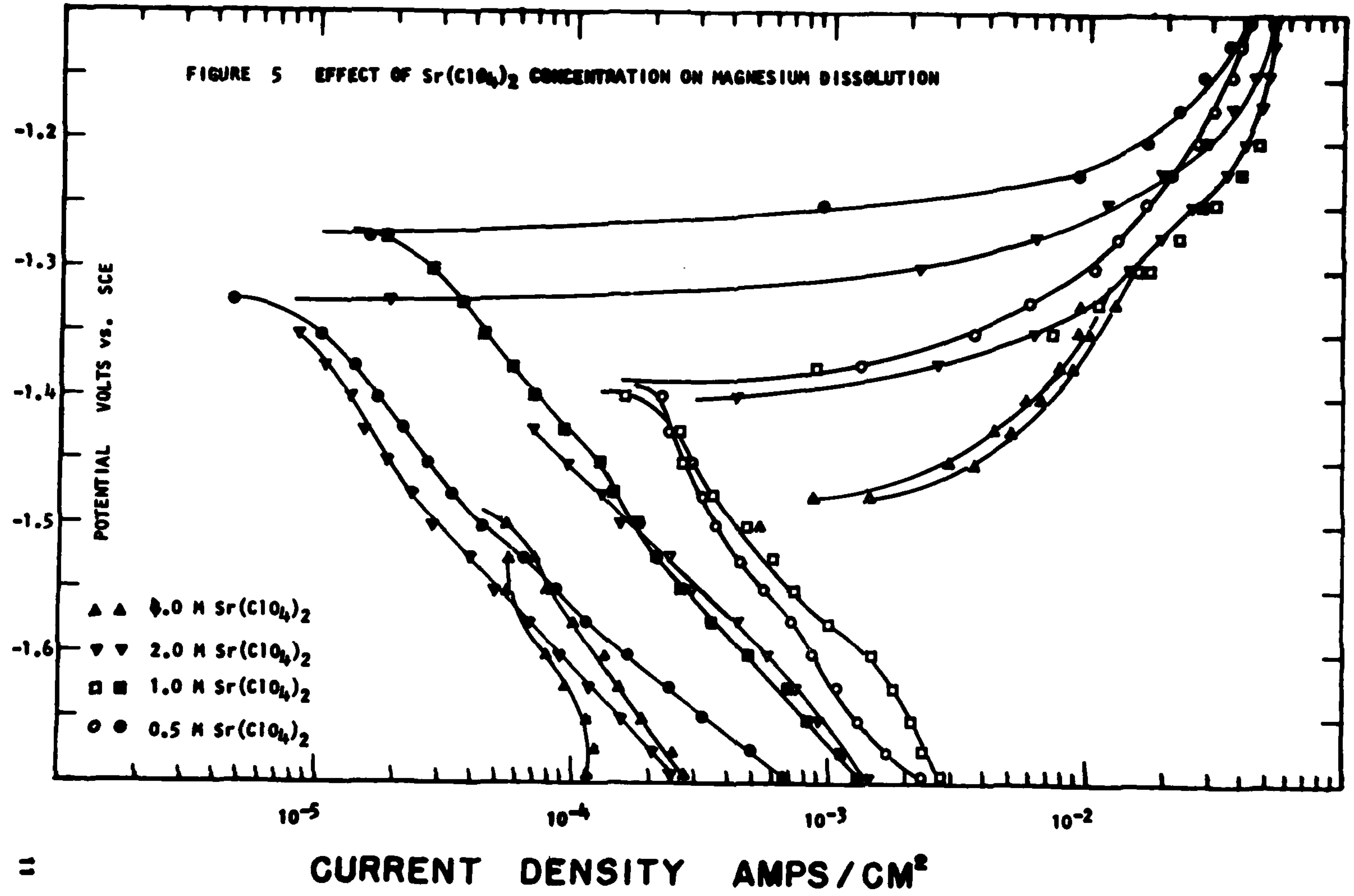


FIGURE 5 EFFECT OF $Sr(ClO_4)_2$ CONCENTRATION ON MAGNESIUM DISSOLUTION

stable corrosion current densities. This phenomena was also observed with $Mg(ClO_4)_2$ electrolytes. From Figure 5 it is seen that the $Sr(ClO_4)_2$ electrolyte would be a relatively poor choice for a magnesium anode battery. The corrosion current density of the magnesium is relatively large and the polarization at reasonable current densities is excessive.

Figure 6 shows the polarization data for the electrochemical reduction of meta-dinitrobenzene in 4M $NaClO_4$ and 2M $Mg(ClO_4)_2$. The polarization curves appear quite similar, but the reaction products appeared to be quite different. In the $NaClO_4$ electrolyte the reaction product was blue in color whereas the reaction product in the $Mg(ClO_4)_2$ was orange in color. At present an analysis of the product is not available.

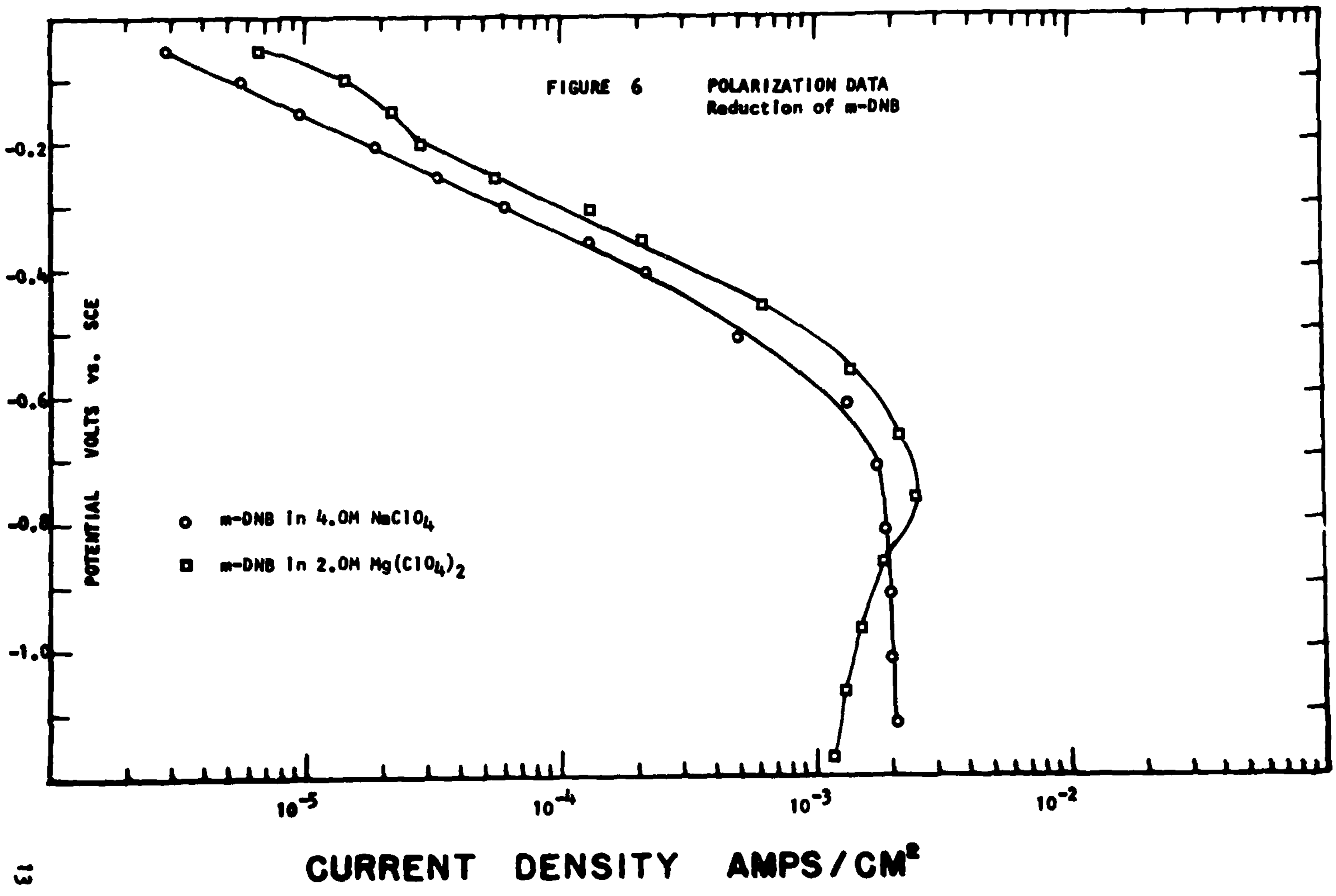


FIGURE 6 POLARIZATION DATA
Reduction of m-DNB

## Conclusion

1. $NaClO_4$ appears to be a better electrolyte than $Mg(ClO_4)_2$ for the Mg-mDNB cell.
2. $Sr(ClO_4)_2$ is an unsatisfactory electrolyte for the Mg-mDNB cell.
3. The rate of reduction of mDNB in $NaClO_4$ and $Mg(ClO_4)_2$ is about equal.
4. The reduction of mDNB appears to yield different reaction products in $NaClO_4$ and $Mg(ClO_4)_2$.

## Recommendations for Future Research

1. Further investigation of the dissolution of magnesium and hydrogen evolution reaction on magnesium in the $NaClO_4$ - $Mg(ClO_4)_2$ electrolyte system.

2. Further investigation of the electrochemical reduction of meta-dinitrobenzene in $NaClO_4$ - $Mg(ClO_4)_2$ electrolyte system.

3. Fabrication of "A" size magnesium - meta-dinitrobenzene cells with 4N $NaClO_4$ electrolyte.

4. Investigation of the dissolution of magnesium, hydrogen evolution reaction on magnesium, and reduction of meta-dinitrobenzene in $LiClO_4$ - $Mg(ClO_4)_2$ and $KClO_4$ - $Mg(ClO_4)_2$ electrolyte systems.

# References

1. L. Wikstrom, "Electrode-Electrolyte Interactions: Magnesium Anode - meta-Dinitrobenzene Cathode", First Semi-Annual Report, ECOM-0143-1, October, 1968.

2. L. Wikstrom, et al., "Electrode-Electrolyte Interactions: Magnesium Anode - meta-Dinitrobenzene Cathode", Second Semi-Annual Report, ECOM-0143-2, August, 1969.

## Identification of Key Personnel

Leonard Lee Wikstrom, Assistant Professor - 1/4 time

Akim Adubifa, Graduate Research Assistant - 1/2 time

Gerald Smaldone, Research Technician - 1/4 time

Unclassified
Security Classification

**DOCUMENT CONTROL DATA - R & D**

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

| | |
|---|---|
| 1. ORIGINATING ACTIVITY (Corporate author)<br>New York University, School of Engineering & Science<br>University Heights<br>Bronx, New York 10453 | 2a. REPORT SECURITY CLASSIFICATION<br>Unclassified<br>2b. GROUP |

3. REPORT TITLE
ELECTRODE-ELECTROLYTE INTERACTIONS MAGNESIUM ANODES::meta-DINITROBENZENE CATHODES

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Semi-Annual 1 Jan 69 to 30 June 69

5. AUTHOR(S) (First name, middle initial, last name)
Wikstrom, J.; A. Adubifa; G. Smaldone; G. Stern

| | | |
|---|---|---|
| 6. REPORT DATE<br>April 1970 | 7a. TOTAL NO. OF PAGES | 7b. NO. OF REFS |

| | |
|---|---|
| 8a. CONTRACT OR GRANT NO.<br>DAAB07-68-C-0143<br>b. PROJECT NO. 1T0 61102 A 34A<br>c. Task No. -02<br>d. Subtask No. -32 | 9a. ORIGINATOR'S REPORT NUMBER(S)<br>9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)<br>ECOM - 0143-3 |

10. DISTRIBUTION STATEMENT
This document is subject to special export controls and each transmittal to foreign Governments or foreign nationals may be made only with prior approval of CG, US Army Electronics Command, Fort Monmouth, N.J. ATTN: AMSEL-KL-PF

| | |
|---|---|
| 11. SUPPLEMENTARY NOTES | 12. SPONSORING MILITARY ACTIVITY<br>Commanding General<br>US Army Electronics Command<br>Fort Monmouth, N.J. ATTN: AMSEL-KL-PF |

13. ABSTRACT

The electrochemical dissolution of magnesium (AZ-21) and hydrogen evolution reaction on magnesium in $Mg(ClO_4)_2$, $Sr(ClO_4)_2$, $NaClO_4$ and $NaClO_4$-$Mg(ClO_4)_2$ electrolyte mix have been investigated. The electrochemical reduction of meta-dinitrobenzene in $NaClO_4$ and $Mg(ClO_4)_2$ has also been studied. Polarization data indicate the corrosion current density of the magnesium electrode is much smaller in the $NaClO_4$ than in the other electrolytes studied. In the $NaClO_4$ - $Mg(ClO_4)_2$ electrolyte mix the corrosion current density of the magnesium electrode increases as the proportion of $Mg(ClO_4)_2$ is increased. In the mixed electrolyte system the magnesium electrode can exhibit two distinctly different corrosion current densities. These corrosion current densities are dependent upon the history of the electrode.

The rate of meta-dinitrobenzene reduction in $NaClO_4$ and $Mg(ClO_4)_2$ was found to be about equal. Even though the reduction rate in the two electrolytes was equal, different reaction products apparently were formed.

DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

Unclassified
Security Classification

| KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| High-Energy Battery Systems | | | | | | |
| Organic Cathode Materials | | | | | | |
| Dinitrobenzene | | | | | | |
| Electroreduction | | | | | | |
| Magnesium Anodes | | | | | | |
| Electrolyte | | | | | | |
| Magnesium Dissolution | | | | | | |