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GALVANOSTATIC VOLTAGE TRANSIENTS OF

MAGNESIUM ANODES

by

Gabriel J. Di Masi

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Electronic Components Laboratory

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U. S. ARMY ELECTRONICS COMMAND

FORT MONMOUTH, N. J.

Abstract

The voltage transient of the magnesium anode has been studied in 2 N and 6 N $Mg(ClO_4)_2$, $MgBr_2$ and $MgCl_2$. In 6 N $Mg(ClO_4)_2$ the transient does not occur when a current is applied. In all other cases the transient polarization (ΔV_{max}) increased with increased applied current, but the transient time ($\mathcal{T}$) decreased. However, one exception is that in 2 N $MgCl_2$ ΔV_{max} increases with current, but $\mathcal{T}$ remains fairly constant.

The effects of pretreating the electrode with a constant anodic current prior to pulsing have also been studied.

CONTENTS

GALVANOSTATIC VOLTAGE TRANSIENTS OF MAGNESIUM ANODES

INTRODUCTION

During the past decade the implementation of magnesium anodes in primary batteries has received considerable attention. Primary cells, utilizing the magnesium anode, have two distinct advantages over batteries with conventional zinc anodes: Increased energy output per unit weight, and a longer shelf life when the corrosion has been greatly reduced. This has generally been achieved by using $MgBr_2$, and $Mg(ClO_4)_2$ electrolytes at 2.0 to 2.5 N containing chromate inhibitors. However, an inherent phenomenon, associated with the magnesium anode is the occurrence of a voltage transient, when a load is applied to the electrochemical cell.

PREVIOUS INVESTIGATIONS

Roald and Beck[1] investigated the dissolution of magnesium in hydrochloric acid solutions ranging from 0.001 to 1.6 molar. They found that the corrosion rate increases both with increased concentration and with increased stirring. The dissolution rate measurements were explained by diffusion, with the proton being the rate-controlling species. Casey and Bergeron[2] measured the rate of corrosion in buffered solutions (at a pH = 2.0) of potassium and magnesium chloride. They found that the dissolution rate depends upon the concentration of the $MgCl_2$ electrolyte at ionic strengths greater than three. The corrosion process is described as a pure proton diffusion aided by internal dissolution of the film with increased concentration of the solution.

Glicksman[3] studied the electrochemical behavior of Mg anodes at a current density of 2 ma/cm^2. The addition of metal ions such as mercurous, lead, aluminum, cadmium, platinum, cupric, and silver to $MgBr_2$ electrolyte changed the potential and the corrosion rate of the magnesium anode. Those metals, having a high exchange current for the hydrogen evolution reaction, accelerated the corrosion rate. Mercury decreases it. Apparently, these metal ions deposit on the electrode to form active centers for the hydrogen evolution reaction. Glicksman reports that the corrosion rate is a linear function of the applied current, and that the overall process is controlled by the diffusion rate of the proton through a porous magnesium oxide-hydroxide film on the anode.

Robinson and King[4] found that when the applied anodic current is greater than the corrosion current, the magnesium electrode exhibits a voltage transient. Increased concentrations of $MgBr_2$ from 1.1 to 5 N decrease this phenomenon; increased currents decrease the transient time, but increase the transient polarization voltage. They explain it as a change in surface coverage that occurs when the Mg ion concentration increases at the anode. Thus, the hydroxyl ion concentration is depleted at the electrode. Thereafter, the halide ions attack the film, and the effective current density decreases, permitting the potential to return to a more negative potential. Recently, King[5] has shown that the proportionality constant relating corrosion to applied current is the transference number of the anion.

In this laboratory experiments[6] have been conducted to reduce the initial transient polarization experienced by magnesium batteries. At the beginning

of the project the transient time of the batteries with an anode area of 6.5 cm^2 discharged under a ten-ohm load to a one-volt cutoff potential was 30 seconds. Increasing the concentration of $Mg(ClO_4)_2$ from 2 to 5 N reduced the transient time to 0.2 seconds but the corrosion rate increased. Thus, to reduce the corrosion the cans were coated with palm oil or other compounds containing fatty acids or esters of fatty acids dissolved in benzene. Optimum results were obtained when a coating solution with one part of palm oil to 17 parts of benzene by weight was used. However, with this battery, designed to reduce the transient, a reduction in the hours of service was obtained.

APPROACH

The experimental investigation of the magnesium anode was conducted principally to determine the factors which affect the voltage transient. It is known from previous work[4] and preliminary studies that electrolyte and electrolyte concentration influence the transient. Therefore, pure magnesium electrodes were studied in electrochemical cells of the type

$$Mg/MgX/Pt$$

in which the anion (X) was either ClO_4^-, Cl^- or Br^- in two or six normal electrolyte concentrations.

Another condition observed in preliminary tests was that a certain amount of electrode corrosion must occur before a transient appears. A further ramification of this condition is that when an anodic current is applied to the magnesium electrode a certain period of zero current should be observed before the voltage transients are measured. When the electrode was in a conditioned state, anodic galvanostatic pulses were impressed on the magnesium electrode to obtain the voltage-time response which included the transient.

Subscribing to the belief that a surface film exists at the electrode, the amount of time (τ) required to reach the maximum transient polarization and ΔV_{max}, which are defined in Fig. 2, were used to characterize the transient. The reason for selecting τ to this point is based on Robinson's[4] data in which he shows that if the current is removed before ΔV_{max} is reached, the potential returns to the open-circuit voltage. Thus, it is probable that there is no significant change in surface coverage before ΔV_{max} is reached. However, when the anodic current is shut off after the potential has passed ΔV_{max}, the electrode becomes temporarily more negative than at open circuit. It is likely that the surface film has been removed under this condition and that it formed again after the anodic current has been shut off.

EXPERIMENTAL PROCEDURE

Commercially pure magnesium electrodes were used in the electrochemical system previously described. The electrode was machined from a magnesium sheet with an area of 6.5 square centimeters. The amount of electrolyte used in each experiment was 75 ± 2 mls.

The cell utilized for these experiments was a three-compartment cell. The working electrode was placed in the center chamber, between two platinum counter electrodes. The two counter electrodes, also in the center, were used to obtain a more even distribution of current at the magnesium electrode. A saturated mercurous sulfate reference electrode we connected to the center chamber through a saturated potassium sulfate salt bridge.

Initially, the electrochemical system was conditioned with constant anodic currents of 1.5 or 15.4 ma/cm² for a period of ten minutes. There was a waiting period of five minutes between the conditioning current and the first anodic pulse, and for each subsequent pulse. The galvanostatic pulses were applied in a sequential order at 3.1, 6.15, 10.8, and 15.4 ma/cm². The experiments were conducted at controlled room conditions (70 ± 2°F, 50% RH).

The measurement of the potential time oscillograms, at constant current, was performed with a triggering circuit (Fig. 1) in which a Tektronix Oscilloscope 561A was used in conjunction with a North Hills precision current source, Model CS-11. The relay was used to switch between the circuit having the 2-ohm load and the electrochemical cell. In this manner, the constant current source was brought to operating conditions using the 2-ohm circuit, eliminating the instrument delay due to warm-up time. Also, the circuit was designed to trigger the oscilloscope when the current transferal occurred. Therefore, a complete galvanostatic pulse which included open circuit, transient, and steady-state voltage was recorded by simply activating the camera shutter.

RESULTS

The voltage transients were compared at galvanostatic pulses of 3.1, 6.15, 10.8, and 15.4 ma/cm². In 6 N $Mg(ClO_4)_2$ (Fig. 5) pure magnesium anode did not have a transient. In all other cases a transient voltage was observed. It was found that an increased galvanostatic pulse current produces a greater ΔV_{max}, but a smaller $\mathcal{T}$ (Fig. 2, 3, 6, & 7). However, one exception occurs in 2 N $MgCl_2$. In this case, an increased pulse current does not change $\mathcal{T}$, though ΔV_{max} increases. It is also pointed out that $\mathcal{T}$ is less than in 2 N $Mg(ClO_4)_2$ and $MgBr_2$.

TABLE I

EFFECTS OF ELECTROLYTE AND CONCENTRATION

APPLIED ANODIC PULSE - 15.4 ma/cm²
PRETREATMENT - 1.5 ma/cm² for 10 Min.

ELECTROLYTE	CONCENTRATION	V_{MAX} (VOLTS)	$\mathcal{T}$ (SEC)
$Mg(ClO_4)_2$	2N	0.28	0.053
	6N	c	0
$MgBr_2$	2N	0.68	0.040
	6N	0.20	0.094
$MgCl_2$	2N	0.20	0.02
	6N	0.30	0.16

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TABLE II

EFFECTS OF ELECTROLYTE AND CONCENTRATION

APPLIED ANODIC PULSE - 10.8 ma/cm^2
PRETREATMENT - 1.5 ma/cm^2 for 10 Min.

ELECTROLYTE	CONCENTRATION	V$_{MAX}$ (VOLTS)	τ (SEC)
Mg(ClO$_4$)$_2$	2N	0.20	0.075
	6N	0	0
MgBr$_2$	2N	0.55	0.05
	6N	0.18	0.14
MgCl$_2$	2N	0.18	0.025
	6N	0.20	0.25

At 2 N concentrations, τ (Tables I & II) decreases according to the electrolyte in this manner

$$\tau_{ClO_4^-} > \tau_{Br^-} > \tau_{Cl^-}$$

and ΔV_{max} is

$$\Delta V_{Br^-} > \Delta V_{ClO_4^-} > \Delta V_{Cl^-}.$$

However, in 6 N solutions the trend is not the same, but shows a complete reversal in which

$$\tau_{Cl^-} > \tau_{Br^-}$$

and

$$\Delta V_{Cl^-} > \Delta V_{Br^-}.$$

Thus, the trend in both τ and ΔV_{max} changes according to the electrolyte concentration.

TABLE III

EFFECTS OF PRETREATMENT CURRENT

APPLIED ANODIC PULSE - 15.4 ma-cm^2
2N CONCENTRATION
PRETREATMENT TIME - 10 Min.

ELECTROLYTE	PRETREATMENT CURRENT DENSITY	V$_{MAX}$ (VOLTS)	τ (SEC)
Mg(ClO$_4$)$_2$	1.5 ma/cm^2	0.28	0.053
	15.4 ma/cm^2	0.20	0.06
MgBr$_2$	1.5 ma/cm^2	0.68	0.04
	15.4 ma/cm^2	0.55	0.08
MgCl$_2$	1.5 ma/cm^2	0.20	0.02
	15.4 ma/cm^2	0.85	2.0

TABLE IV

EFFECTS OF PRETREATMENT CURRENT

APPLIED ANODIC PULSE - 15.4 ma/cm^2
6N CONCENTRATION
PRETREATMENT TIME - 10 Min.

ELECTROLYTE	PRETREATMENT CURRENT DENSITY	V_{MAX} (VOLTS)	Υ (SEC)
$Mg(ClO_4)_2$	1.5 ma/cm^2	0	0
	15.4 ma/cm^2	0	0
$MgBr_2$	1.5 ma/cm^2	0.18	0.14
	15.4 ma/cm^2	0.15	0.09
$MgCl_2$	1.5 ma/cm^2	0.20	0.25
	15.4 ma/cm^2	0.12	0.12

The effects of pretreatment current are presented in Tables III and
IV. In all cases at 2 N for a pretreatment time of ten minutes, the delay
time at the higher pretreatment current is greater than at the lower, but
ΔV_{max} does not show a constant trend. In 6 N electrolytes a reverse trend
is observed whereas Υ decreases at the higher pretreatment current.

DISCUSSION OF RESULTS

The effects of current density, electrolyte, concentration, and pre-
treatment are reproducible and have a maximum deviation of $\pm$ 5%. The
general effects of current density on Υ and ΔV_{max} give greater evidence for
accepting the dissolution of the anodic film as the controlling process
before a steady-state potential is reached. The mechanism which describes
this film breakdown has not been established.

The effects of anion and concentration are presented, but no comments
as to the significance of the results can be made without further study.
Pretreating the magnesium electrode with an anodic constant current has
produced results which may be partially the effects of pH. Calculations
have shown that at pretreatment current densities of 1.54 and 15.4 ma/cm^2
excessive amounts of hydroxyl ions are formed causing $Mg(OH)_2$ to precipitate.
This is the case, both in 2 N electrolytes at pH = 8.45 and in 6 N electro-
lytes at pH $\approx$ 8.24. During pretreatment at open-circuit potential a $Mg(OH)_2$
film is formed by corrosion. This film is not formed during the anodic
pretreatment because transients were observed only after a waiting period
at open circuit potential.

RECOMMENDATIONS

1. A study of the pH effects on the voltage transient should be
undertaken. These measurements should be correlated with the corrosion rate
and the corrosion pattern at the magnesium anode. Estimates of the surface
roughness should also be made.

2. To determine the effects of diffusion on the transient, the electrolyte should be stirred.

3. Glickman[3] has found that amalgamating magnesium with small quantities of mercury reduces its corrosion rate. Since corrosion initiates conditions favorable for the occurrence of the transient a less corrosive electrode should be explored.

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3. R. Glickman, "Electrochemical Society Journal," 106, 83 (1959).

4. J. L. Robinson and P. F. King, "Electrochemical Society Journal," 108, 36 (1961).

5. P. F. King, "Electrochemical Society Journal," 113, 536 (1966).

6. D. Wood and J. Hovendon, "Magnesium Dry Cell Batteries," Power Sources Conference, 19th Annual Proceedings (May 1965).
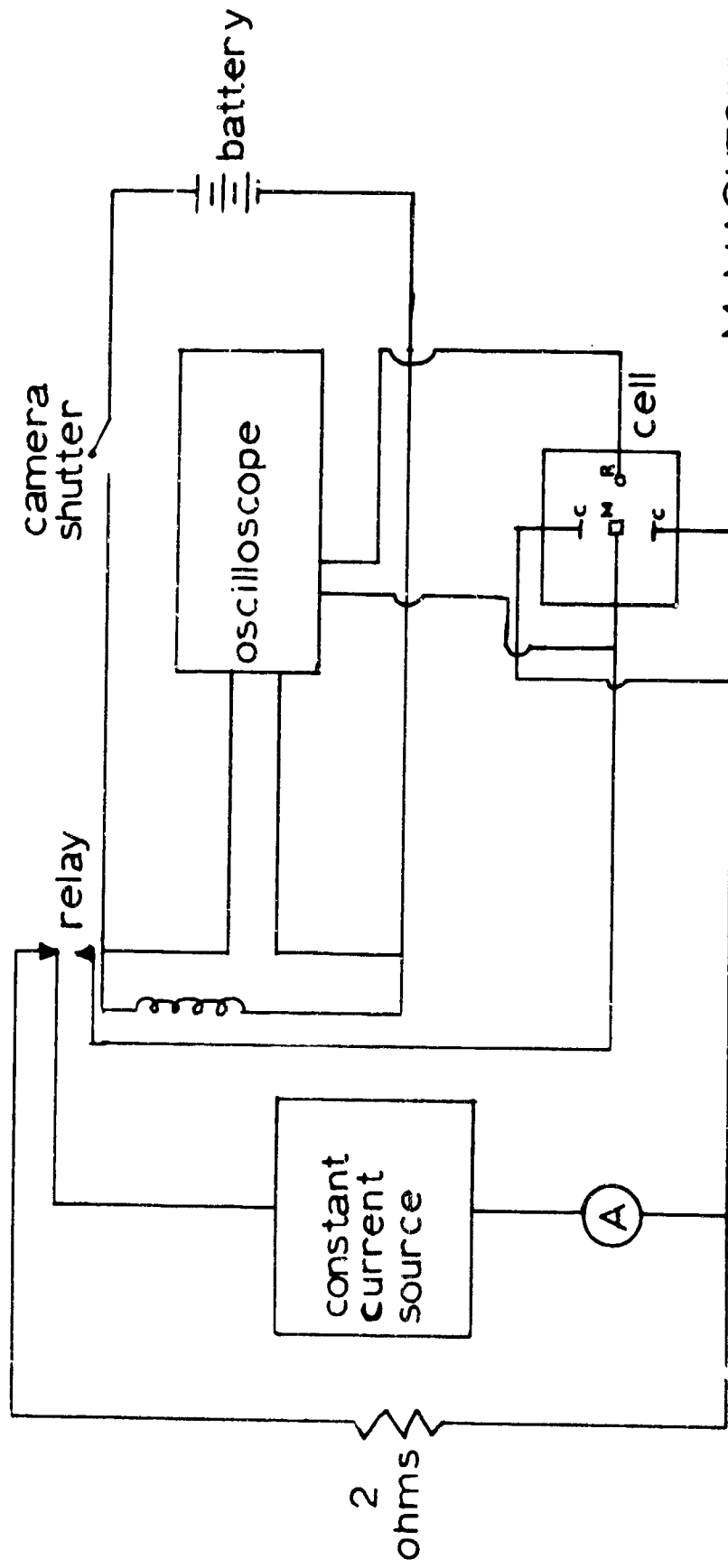
M-MAGNESIUM ANODE
C-COUNTER ELECTRODE
R-REFERENCE ELECTRODE

FIG.1 CONSTANT CURRENT TRIGGERING CIRCUIT

ANODIC VOLTAGE TRANSIENTS
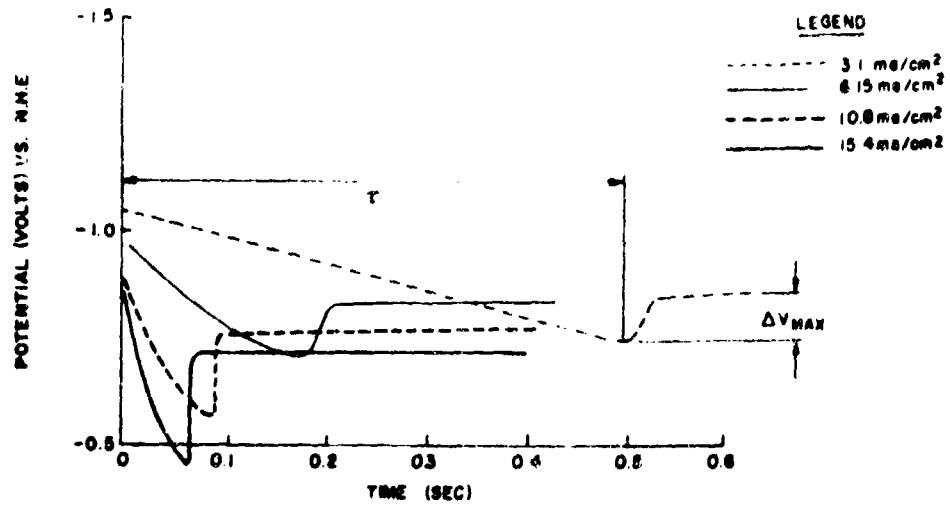PURE Mg - 2N ELECTROLYTE
PRETREATMENT -15 ma/cm2 FOR 10 MIN.
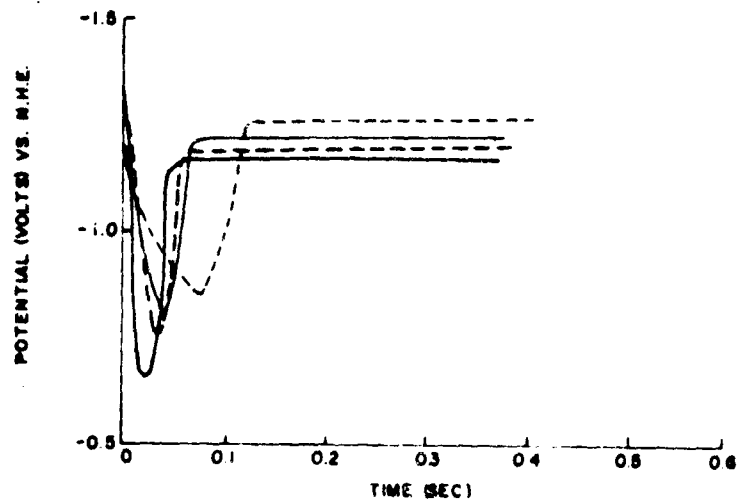

FIG.2   Mg(ClO₄)₂
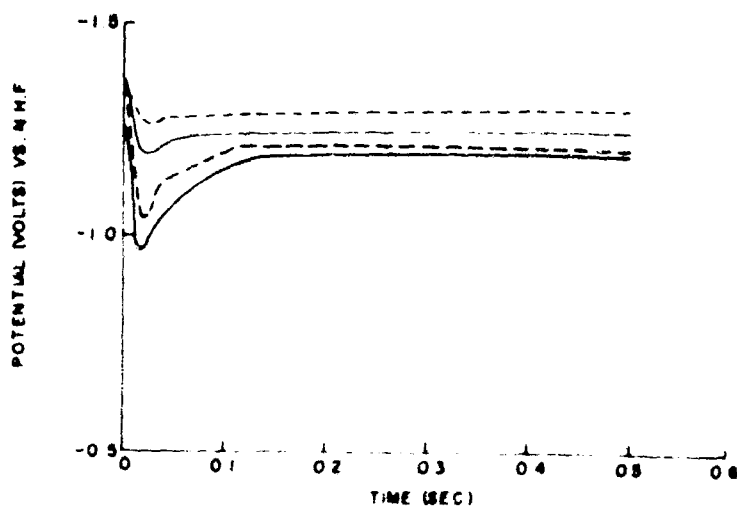
O.C.V.=-1.11 VOLTS

FIG 3   MgBr₂

O CV =-133 VOLTS

FIG 4 MgCl₂

O CV =-143 VOLTS

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ANODIC VOLTAGE TRANSIENTS
PURE Mg-6N ELECTROLYTE
PRETREATMENT — 1.8 ma/cm² FOR 10 MIN.

LEGEND
- - - - - - 3.1 ma/cm²
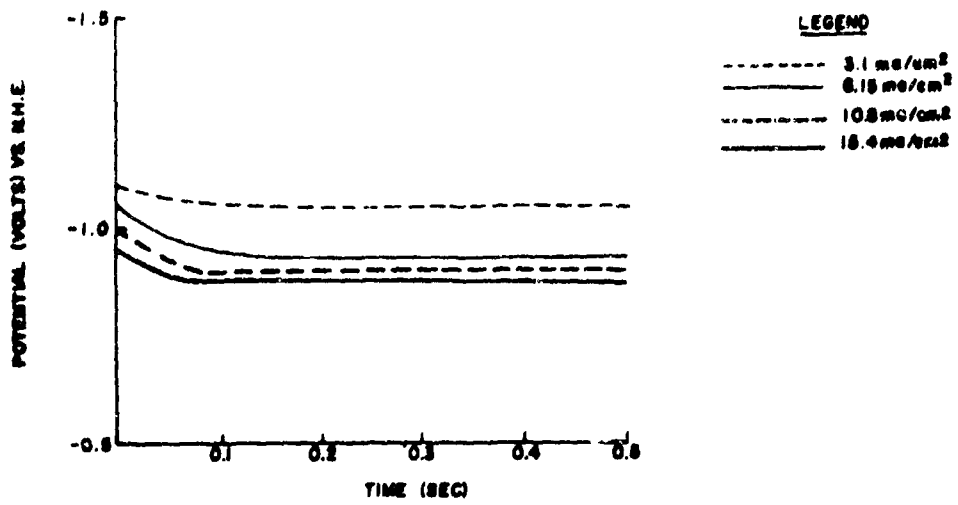———— 6.15 ma/cm²
- - - - - 10.8 ma/cm²
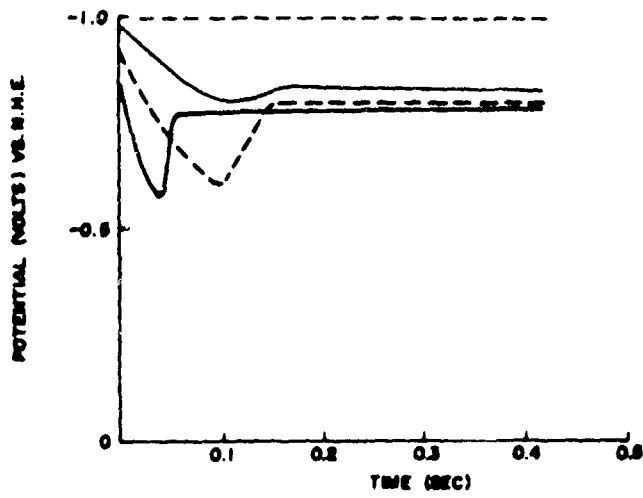———— 15.4 ma/cm²

FIG.5   Mg(ClO₄)₂
O.C.V. = -1.2 VOLTS

FIG.6   Mg Br₂
O.C.V. = -1.06 VOLTS

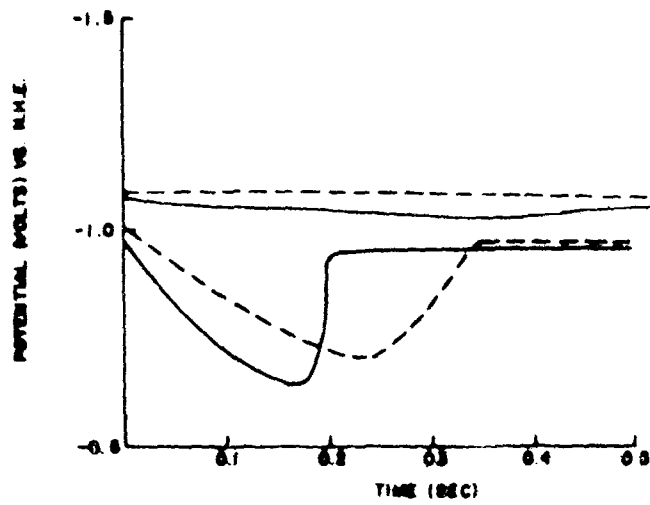FIG.7   Mg Cl₂
O.C.V. = -1.13 VOLTS

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13 ABSTRACT

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