

Second Quarterly Report
Research & Development

on

Electrodeposited Inorganic Separators

15 July 1965 - 15 October 1965

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General Electric Company
Research and Development Center
Schenectady, New York

for

NASA

Goddard Space Flight Center
Greenbelt, Maryland

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SUMMARY

The objective of this program is to evaluate the use of thin electrodeposited films of calcium and magnesium hydroxides as separators in silver - cadmium cells. Potential gains to be made with the successful development of these separators are increased thermal stability at elevated temperature and a reduction in silver migration.

During this quarter the work was continued on studying the effect of processing parameters on deposition rate and film properties as well as conducting preliminary tests with cells to determine the effect of sterilizing coated electrodes at 145°C. The process studies₂ showed that over the range of current densities investigated (200-1000 ma/in²) the calcium hydroxide films are more adherent and uniform than the magnesium hydroxide films when using an electrolyte concentration of 70 g/l of the respective acetates for coating. Improvements in the uniformity and adherence of magnesium hydroxide films were obtained by increasing the magnesium acetate concentration to approximately 450 g/l.

Sterilization tests on calcium hydroxide coated silver electrodes show that the electrodes can be sterilized for at least two periods of 40 hours at 145°C without significant loss of coating. Charge-discharge cycling tests after sterilization show that some of the electrodes develop their nominal capacity in three to four cycles when charged at c/5 rates and discharged at c/2.5 rates. Unsterilized coated electrodes, in all cases tested, developed their nominal capacity within two to three cycles under similar conditions. Retention of the coatings after short term cycling (6 cycles) and sterilization in most cases was good.

1.0 INTRODUCTION

This report covers the work done during the second quarter of a 12-month program to evaluate the use of thin electrodeposited films of calcium and magnesium hydroxide as separators in silver-cadmium cells. The potential advantages to be gained in using these separators are an increase in chemical stability of the cell separators at elevated temperature and a reduction in silver migration.

The objective of the program is twofold: first, to determine the effect of process parameters on the thickness, porosity and adherence of the films on representative silver and cadmium electrodes, and second, to evaluate the performance of these films in single cells in terms of electrolyte retention, internal cell resistance, charge-discharge characteristics, control of silver transport, and stability at elevated temperatures.

During the second quarter process studies were continued to determine the rates of film deposition for both calcium and magnesium hydroxides on discharged silver electrodes. Parameters investigated were current density, electrolyte concentration and deposition time, all at ambient temperature. Coating characteristics determined were weight gain, coating thickness, and resistance increase contributed by the films in 31 percent by weight potassium hydroxide solutions. Coated silver electrodes were sterilized at 145°C for periods of forty hours and were then fabricated into test cells to evaluate the electrochemical performance obtained compared to unsterilized coated electrodes.

2.0 DISCUSSION OF EXPERIMENTAL RESULTS

The emphasis during the second quarter was on a study of the parameters affecting the deposition process for both calcium and magnesium hydroxides and the continued evaluation of sterilized and unsterilized coated electrodes in tests cells.

2.1 Process Parameter Studies

2.1.1 Calcium Hydroxide

For the calcium hydroxide coatings the effect of current density over the range of 200-1000 ma/in² were investigated using two electrolyte systems. The electrolyte in one case consisted of a solution of 70 g/l of calcium acetate saturated with calcium hydroxide from which the excess solid calcium hydroxide was filtered. The above electrolyte was used for one coating run and then buffered with one gram of calcium hydroxide for the second coating run. Fresh solutions were used for each coating time at a given current density. The intent of these experiments was to determine if the depletion of calcium ion and shifting of pH of the solution was a significant factor in a given run. The volume of solution used in these tests was one liter. The silver electrodes used in the coating experiments were from Yarney Model YS5(50-4 "Silcal" cells. Unless otherwise indicated the electrodes were cut in half for these tests and had nominal dimensions of 13/16 by 1 1/2 inches.

The general procedure for coating was the same as described in the first quarterly report except for the following change. For a given current density and coating time a fresh volume of electrolyte was used. After the first run was made, one gram of calcium hydroxide was added to the electrolyte prior to making the second run at the same conditions.

The results of these runs comparing weight gains, film thicknesses, and resistance increases are shown in Figures 2.1 through 2.4. The numerical data for these figures are summarized in Appendix A. The effect of the solid excess calcium hydroxide in the electrolyte did not appear to be significant at short coating times. At the longer coating times there was some evidence that buffering with calcium hydroxide improved the coating process efficiency. At the lower current densities (200 and 400 ma/in²) the deposition efficiency decreases and reproducibility of coatings and uniformity is poorer compared to the higher current densities.

The greatest source of variation is found in the 1000 cps resistance gain values. These measurements are made with a 1000 cps bridge. The procedure used was to first measure the total resistance of the uncoated electrodes in a cell containing 31 percent by weight potassium hydroxide against an inert electrode at three fixed separations between the electrodes, 0.5, 1.0, and 1.5 inches. These values were extrapolated to a separation distance of zero,

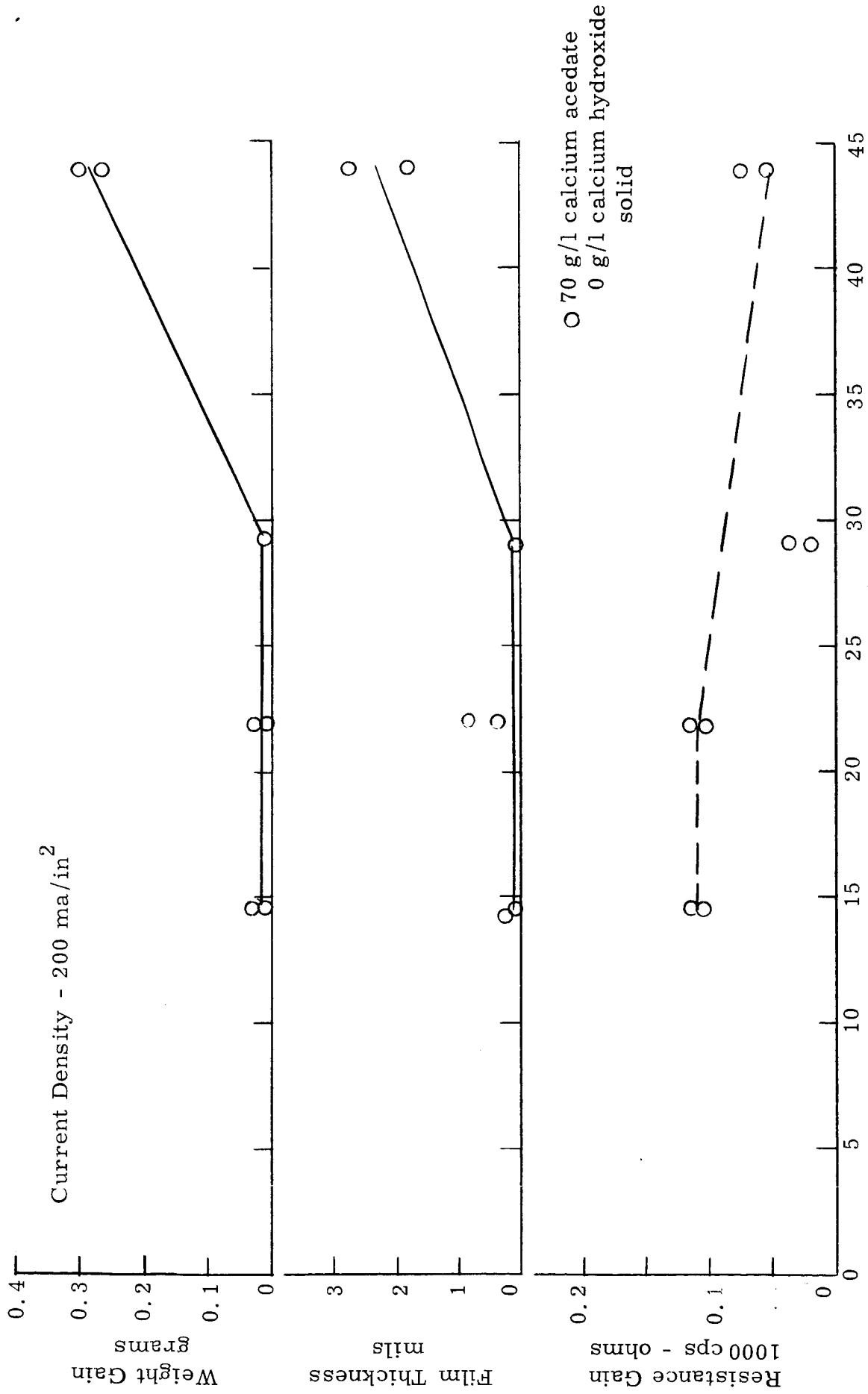


Figure 2-1. Calcium Hydroxide Films on Discharged Silver Plates
Plates 13/16" x 24/16" From - YS5(S)-4 Cells

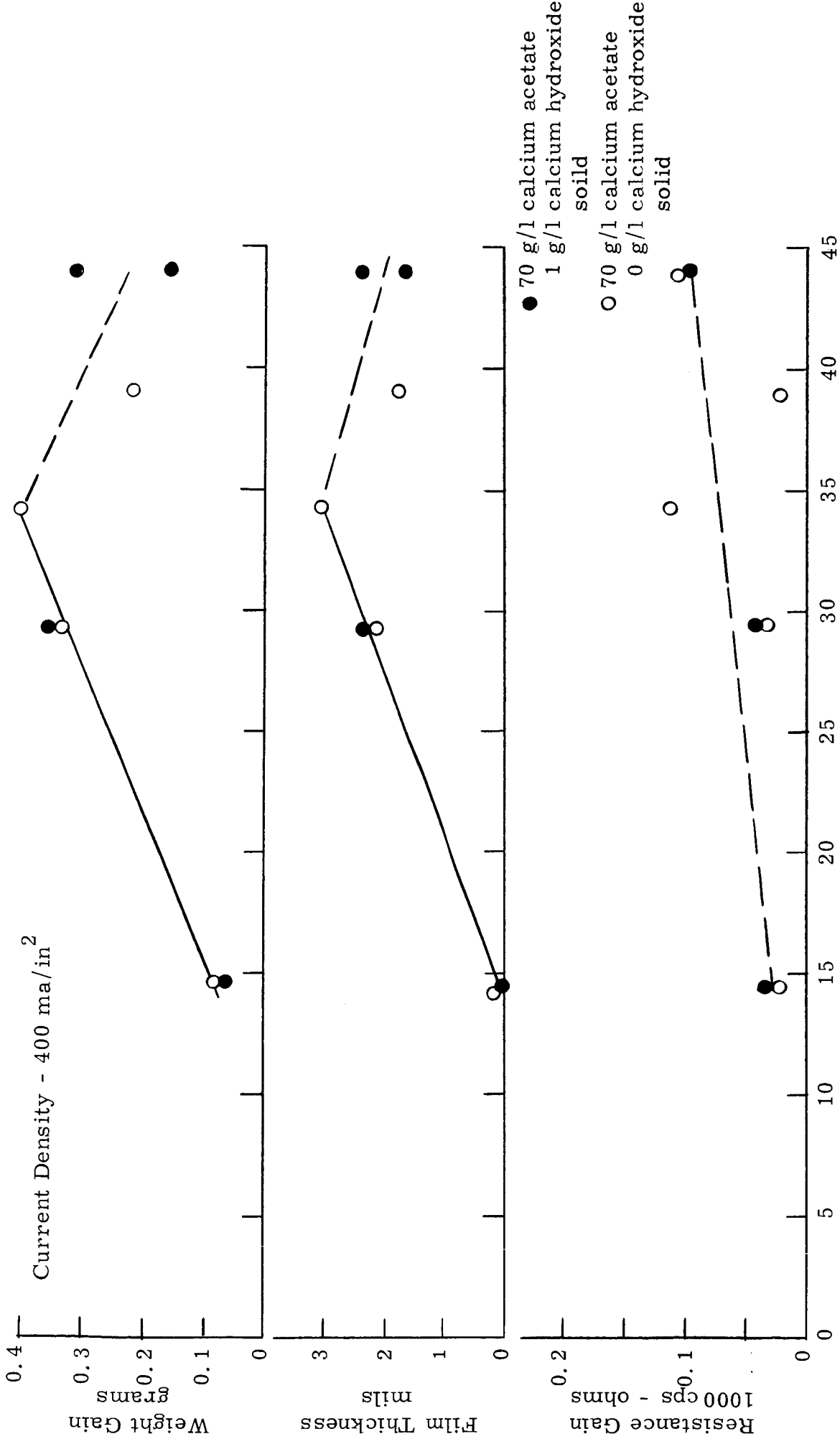


Figure 2-2. Calcium Hydroxide Films on Discharged Silver Plates
Plates 13/16" x 24/16" From YS5(S)-4 Cells

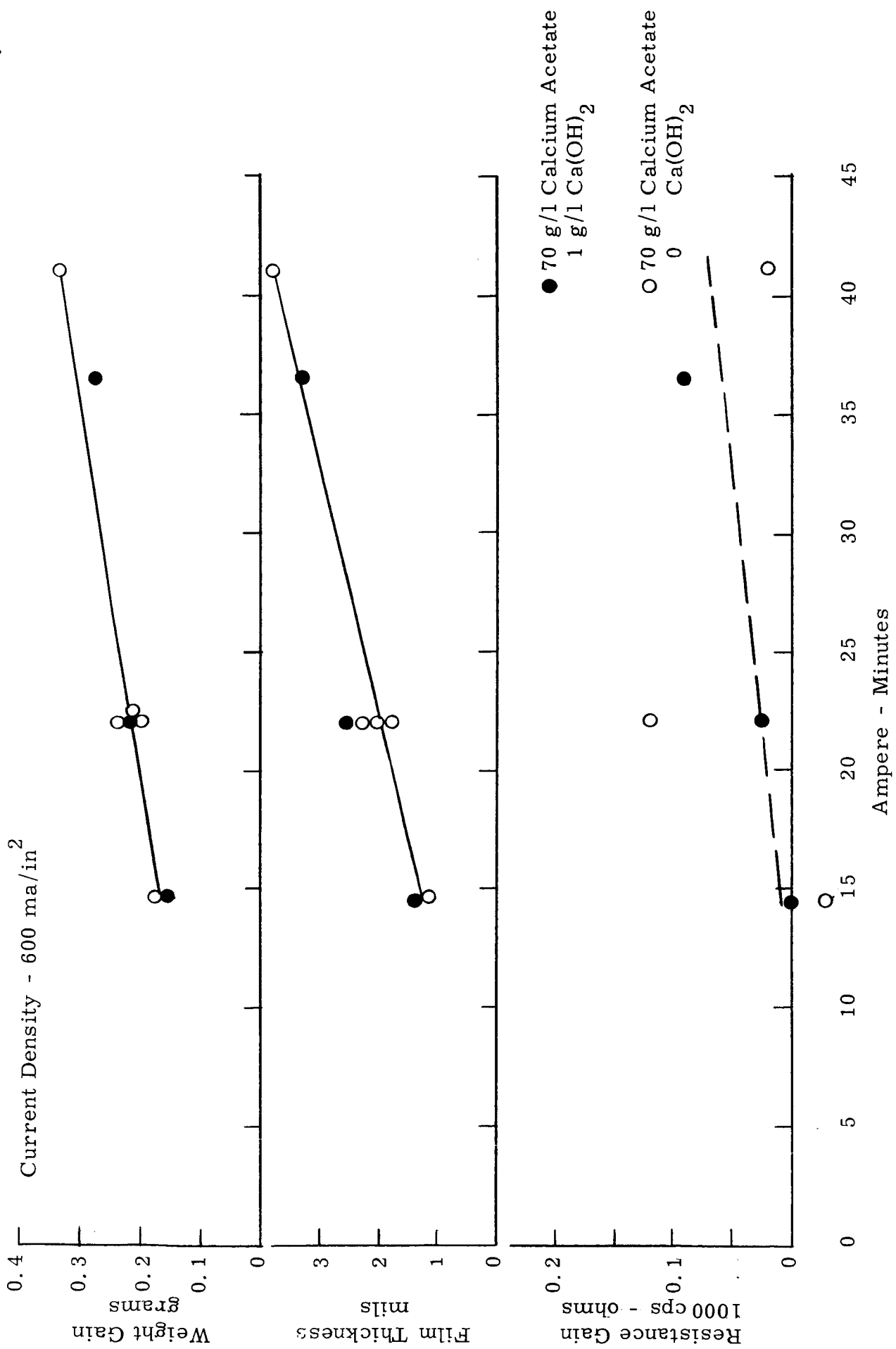


Figure 2-3. Calcium Hydroxide Films on Discharged Silver Plates: Plates - 13/16" x 24/16" - From YS5(S)-4 Cells.

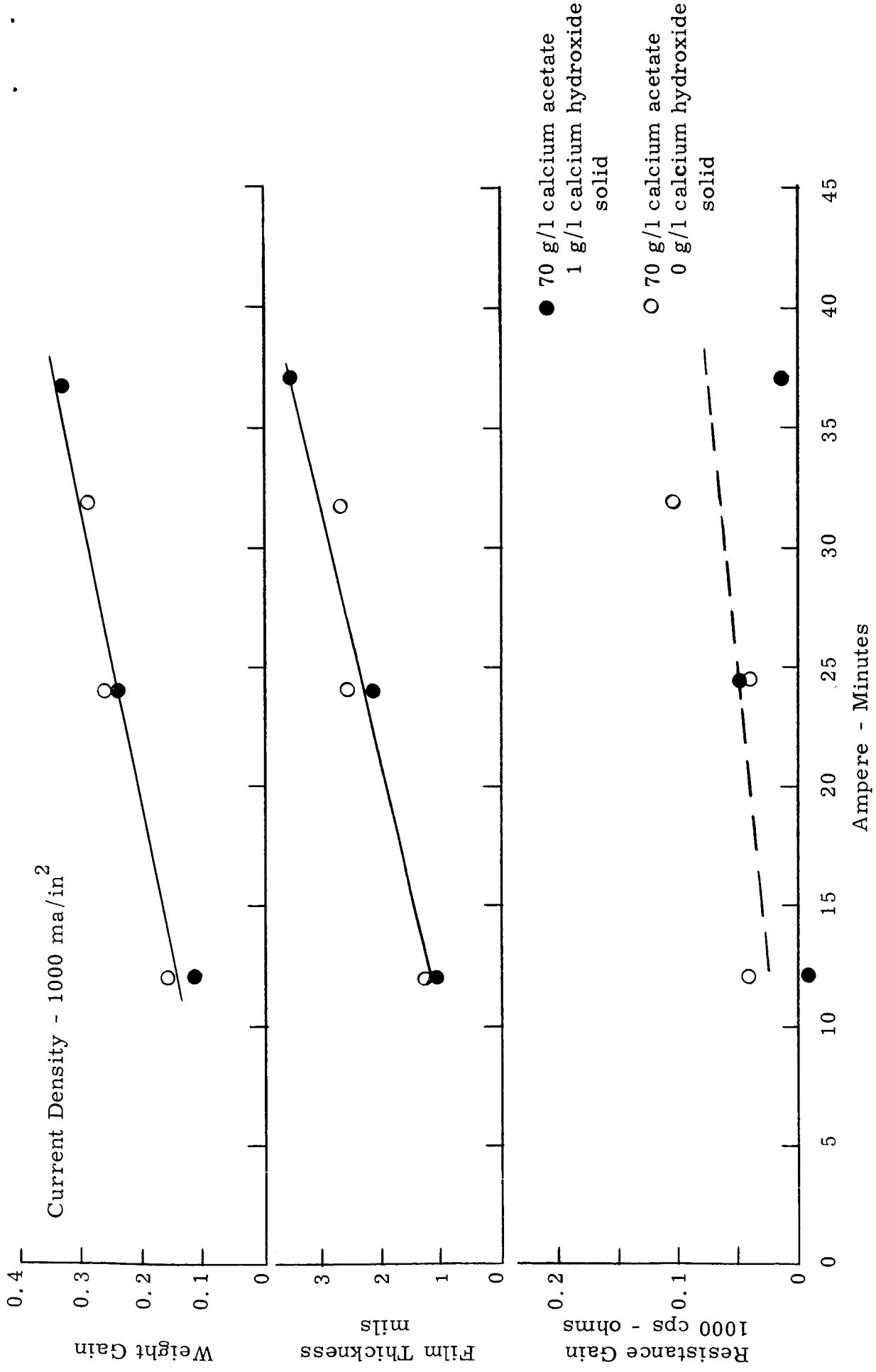


Figure 2-4. Calcium Hydroxide Films on Discharged Silver Plates
Plates - 13/16" x 24/16" - From YS5(S)-4 Cells

to give the effective resistance of the electrode structure electrolyte interface. This measurement and extrapolation procedure was repeated on the coated electrodes. The resistance gain values plotted in the figures is the difference in the extrapolated values at zero separation before and after coating.

The uncoated electrodes show considerable variations in values ranging from 0.07 to 0.21 ohms for plates of $13/16'' \times 1\ 1/2''$. In some instances the extrapolated resistance values obtained after coating were lower than the original uncoated electrode resistance value. Part of this variation in the case of the uncoated electrodes appears to be dependent on the penetration of the electrolyte into the pores. Measurements taken over various periods of time (several hours) show that within a few hours the readings approach a stable value.

The uniformity of these coatings based on microscopic observations and micrometer thickness measurements is good. The adherence qualitatively is good. No quantitative adherence tests have been performed.

In view of the variability in resistance values it appears desirable to investigate this area in more detail. One obvious approach is to work the electrodes through one or more charge-discharge cycles noting the effect on resistance change and also for improved consistency on subsequent coating. A further area of study should include the deposition of films on charged electrodes to compare adherence as well as resistance values.

2.1.2 Magnesium Hydroxide

For the magnesium hydroxide coatings additional runs were made to determine conditions which would yield more uniform and adherent coatings than were obtained in the first quarter. An electrolyte concentration of 70 grams per liter of magnesium acetate was used in the first set of runs. Over the range of current densities from 25 to 200 ma/in² negligible film thickness buildups were obtained with coating times of 30 minutes. The presence of excess magnesium hydroxide did not make any appreciable difference in the results. What coatings that were obtained were poorly adhering and spotty in coverage of the electrode surface.

The effect of magnesium acetate concentration was investigated at the following levels, 20, 35, 70, and approximately 450 g/l. A summary of the runs made and the resulting data are given in Appendix B. At the highest concentration level significant film thicknesses were obtained using current densities of 100 and 200 ma/in² and deposition times of 60 minutes. The films were spotty in coverage. It appears that the shiny and smooth metallic areas especially in the regions of the metallic grids used in the electrodes are not coated. Much of the coating is sloughed off when immersed in 31 % potassium hydroxide to make the electrode resistance measurements. However, the electrodes did have an adhering residual film which was insulating when measured with an ohmmeter.

A few more coating experiments will be made during the next quarter on electrodes which have been worked through a charge-discharge cycle and also on charged electrodes. In view of the better overall results obtained with calcium hydroxide coatings, major emphasis in the future coating work will be on the calcium hydroxide coatings.

2.2 Sterilization Test Results

The effect of sterilization on the charge-discharge performance over four to six complete cycles was determined for a number of calcium hydroxide coated silver electrodes. These electrodes were selected from the coating experiments described in the previous section of this report. Samples of electrodes were taken at each of the current density levels studied. The electrodes selected had film thicknesses of approximately 2 mils. Comparative tests were made with unsterilized coated electrodes. The identification of the electrodes is given in Table 2-1. The details of experimental sequence, results, and other observations are given below.

A preliminary sterilization experiment was made with electrodes numbered 1 and 2 by immersing the electrodes in an open beaker containing 31% potassium hydroxide and allowing the solution to boil. Replenishment of the solution with distilled water was made from time to time, however, overnight the solution evaporated to dryness. The total exposure at elevated temperature was 29 hours. The electrodes were then soaked in distilled water for a one week period to insure removal of potassium hydroxide residues. Thickness, weight, and resistance measurements showed some decrease. It was decided to recoat these electrodes and then to repeat the sterilization in a bomb to eliminate the evaporation of the electrolyte. The coating conditions employed were 200 ma/in² for 30 minutes. The electrodes were then sterilized at 145°C for a period of 40 hours.

The electrodes were then assembled into an open flooded test cell using two sintered matrix cadmium counterelectrodes. Electrode separation was maintained by an open mesh plastic webbing.

The cells were cycled six times using a constant current charge rate of $c/5$ and $c/2.5$ for discharge. The nominal capacity of one ampere hour was obtained for both electrodes on the fourth cycle and continued for the fifth and sixth cycle when the test was terminated. Charge potentials started at about 1.6 volts and increased to 2.0 volts for most of the charge period. The discharge potentials started at 1.2 volts and decreased to approximately 0.9 volts for most of the discharge cycle.

The electrodes were resterilized in a bomb for another 40 hour period at 145°C and then returned to the cyclic tests as described above. Both electrodes yielded their nominal one ampere-hour capacity on the fourth cycle. Voltage behavior during charge and discharge was the same as in the first set of cyclic tests.

TABLE 2 - 1
Sterilization and Cyclic Test Summary for Calcium Hydroxide Coated Silver Electrodes

Electrode Number	Coating		Test Sequence
	Density (ma/in ²)	Initial Coating Thickness (mils)	
<u>Full Size Electrodes</u>			
1	200	2.5	(a) Open beaker sterilization in boiling 31% KOH, 29 hours, followed by recoating
2	200	2.5	(b) Sterilized inclosed bomb for 40 hours @ c/2.5 rate for 6 cycles (c) Sterilized as in (b) followed by 4 cycles as in (b)
<u>Half Size Electrodes</u>			
921-5	400	2.3	(d) Unsterilized - 6 cycles as in (b)
921-6	400	2.2	(e) Sterilized and cycled as in (b)
1018-2	600	1.8	(f) Unsterilized - 4 cycles as in (b)
1018-1	600	2.0	(g) Sterilized and 4 cycles as in (b)
1011-3	1000	2.5	(h) Unsterilized - 4 cycles as in (b)
1011-4	1000	2.5	(i) Sterilized and 4 cycles as in (b)

Note: See text, Section 2.1 for results.

A check of the electrode-electrolyte resistances was made during the course of the sterilization tests and after the cycling tests. In each case electrode resistances increased as a result of sterilization and decreased as a result of the cycling. There were corresponding weight and thickness increases as a result of sterilization and some decrease after the cycling tests. In part these changes were probably caused by incomplete removal of potassium hydroxide adsorbed and dried in the electrodes as the measurements were made. Another known contributing factor was the fact that during the sterilization tests some silica from the glass beakers was dissolved in the electrolyte.

Point to point surface resistance measurements made during the course of and after completion of the tests showed that electrodes were coated with an insulating film. Microscopic examinations of the electrodes after the test showed that some areas of the electrodes were covered with a relatively thick opaque white coating similar to the original coating and other areas had a thinner translucent residual film.

In sterilizing the remaining electrodes a teflon beaker was used to eliminate the problem of silica dissolution.

For the remaining electrodes listed in Table 2-1, one electrode at each coating current density was sterilized for one period of 40 hours at 145°C. These electrodes were then assembled into test cells, as were the corresponding unsterilized electrodes and cycled as described above.

The nominal capacity of the unsterilized electrodes developed within two or three cycles. The sterilized electrodes in the case of electrodes coated at 400 and 600 ma/in² failed to develop any capacity over the number of cycles listed in Table 2-1. The sterilized electrode coated at 1000 ma/in² showed a capacity of less than 10% of the nominal one ampere-hour capacity after the third cycle.

The 1000 cps electrode-electrolyte resistance values taken after sterilization showed an increase over the value obtained after the coating was made. Values of measurements made after cycling in all cases were less than the values before cycling. However, in some cases the values were less than the original uncoated values and in others the values were in between the original coated and uncoated values.

Point to point resistance measurements across the surface of the electrodes after the cyclic tests showed the presence of an insulating film on all electrodes. In general the unsterilized electrode resistance values were lower than for the sterilized electrodes.

Microscopic examinations of the electrodes showed variability of the thickness, and opacity of the films. Generally the unsterilized electrodes showed greater areas of thinner and more translucent films than the sterilized electrodes.

On the basis of these results it appears that some dissolution or loosening of the coating in the internal pore structures of the electrodes must occur for the electrodes to accept charge and develop capacity.

Factors which contributed to some of the sterilized electrodes accepting charge and developing the full capacity while others did not are not clearly identifiable from the set experiments performed to date. An unknown factor is the effect of dissolved silica which occurred in sterilizing the first set of electrodes.

On the basis of these tests, developing cells capable of withstanding sterilization at 145°C for several cycles of 40 hours duration appears promising. Further work is needed to determine the variability noted in charge acceptance.

3.0 PROGRAM FOR NEXT QUARTER

Full size electrodes will be coated and the migration of silver will be studied in single electrode and cell experiments. Some five ampere-hour cells will be modified with coated silver electrodes and put on cyclic charge-discharge tests. Additional process parameter studies will be done with emphasis on coating cycle discharged and charge silver electrodes.

APPENDIX A

Calcium Hydroxide Film Data

APPENDIX A

Summary of Film Deposition Data for Calcium Acetate Electrolyte

Sample No.	Acetate Concentrations (g/l)	Hydroxide Concentrations (g/l)	Current Density (ma/in ²)	Current Density (ma)	Time (min)	Initial Voltage (volts)	Voltage (volts)	Weight Gain (grams)	Thickness of Film per Side (mils)	1000 cps Resistance Extrapolated Values	
										Before Coating (ohms)	After Coating (ohms)
9/17 1	70	-	200	488	30	3.9	5.8	0.005	0.05	0.092	0.210
9/17 2	70	-	200	488	30	3.5	6.3	0.006	0.05	0.105	0.210
9/17 3	70	-	200	488	45	3.2	7.8	0.054	0.4	0.085	0.210
9/17 4	70	-	200	488	45	3.1	8.4	0.096	0.9	0.105	0.210
9/17 5	70	-	200	488	60	3.3	13	0.013	0	0.088	0.122
9/17 6	70	-	200	488	60	3.2	9.6	0.010	0	0.088	0.112
9/17 7	70	-	200	488	90	3.4	46	0.306	2.8	0.088	0.142
9/17 8	70	-	200	488	90	3.45	39	0.272	1.9	0.088	0.162
9/21 1	70	1	400	976	45	4.7	50	0.155	1.6	0.080	0.170
9/21 2	70	-	400	976	40	3.9	50	0.217	1.75	0.090	0.110
9/21 3	70	1	400	976	15	3.9	8.4	0.065	0	0.080	0.110
9/21 4	70	-	400	976	15	3.9	8.6	0.067	0	0.080	0.100
9/21 5	70	1	400	976	30	4.1	18.6	0.354	2.3	0.072	0.100
9/21 6	70	-	400	976	30	3.9	16.3	0.330	2.2	0.080	0.110
9/21 7	70	1	400	976	45	4.1	46	0.382	2.3	0.080	0.170
9/21 8	70	-	400	976	35	3.9	47.5	0.409	3	0.080	0.190
10/4 1	70	1	600	1465	15	6.5	23	0.233	2.4	0.183	0.210
10/4 2	70	-	600	1465	15	5.7	21	0.227	2.2	0.170	0.290
10/4 3	70	1	600	1465	25	4.9	40	0.279	3.3	0.170	0.262
10/4 4	70	-	600	1465	28	4.8	42	0.341	3.8	0.170	0.190
10/4 5	70	1	600	1465	10	5.4	8.9	0.165	1.3	0.170	0.170
10/4 6	70	-	600	1465	10	5.1	9.05	0.170	1.35	0.183	0.150
10/11 1	70	-	1000	2440	5	7.5	19.6	0.151	1.15	0.170	0.210
10/11 2	70	1	1000	2440	5	6.9	16.8	0.123	1.05	0.193	0.180
10/11 3	70	-	1000	2440	10	7.4	31.5	0.252	2.55	0.170	0.210
10/11 4	70	1	1000	2440	10	7.1	24.5	0.252	2.1	0.208	0.250
10/11 5	70	-	1000	2440	13	7.4	42	0.290	2.6	0.175	0.280
10/11 6	70	1	1000	2440	15	6.8	22.5	0.337	3.55	0.198	0.210
10/18 1	70	-	600	1465	15	5.1	11	0.206	1.75	0.172	0.250
10/18 2	70	-	600	1465	15	5.2	14	0.215	2.0	0.172	0.260

APPENDIX B

Magnesium Hydroxide Film Data

APPENDIX B

Summary of Film Deposition Data for Magnesium Acetate Electrolyte

Sample No.	Acetate Concentrations (g/l)	Hydroxide Concentrations (g/l)	Current Density (ma/in ²)	Current Density (ma)	Time (min)	Initial Voltage (volts)	Voltage (volts)	Weight Gain (grams)	Thickness of Film per Side (mils)	1000 cps Resistance Extrapolated Values	
										Before Coating (ohms)	After Coating (ohms)
10/19 1	70	-	50	122	30	1.6	2.83	0.084	0.3	0.193	-
10/19 2	70	1	50	122	30	1.9	2.5	0.091	0.15	0.193	-
10/19 3	70	-	25	61	30	1.75	2.08	0.081	0.1	0.193	-
10/19 4	70	1	25	61	60	1.7	2.22	0.099	0.05	0.193	-
10/19 5	35	-	25	61	90	1.7	2.32	0.106	0.05	0.193	-
10/19 6	35	1	25	61	90	1.6	2.28	0.080	0	0.172	-
10/19 1*	70	-	200	488	30	3.3	3.85	0.010	0.25	0.193	-
10/19 2*	70	1	200	488	120	2.75	3.46	0.054	0.4	0.193	-
10/19 3*	35	-	100	244	60	2.8	3.45	0.016	0.6	0.193	0.134
10/19 4*	35	1	100	244	60	2.6	3.34	0.015	0.35	0.193	0.142
10/19 5*	35	-	200	488	90	3.0	4.25	0.005	0.90	0.193	0.102
10/19 6*	35	1	200	488	60	3.1	4.24	0	0.85	0.193	0.120
10/19 1*	20	1	100	244	60	3.95	4.25	- .038	- .2	-	0.120
10/19 2*	20	-	100	244	60	4	4.3	- .054	- .1	-	0.120
**=rerun											
11/11 1	450	-*	100	244	150	2.1	3.32	0.128	2.85	0.200	0.080
11/11 2	450	-	200	488	60	3.8	4.3	0.161	2.1	0.230	0.130
*C-OC prior to coat											
10/28 1	140	-	50	122	60	2	2.80	0.100	0.4	0.132	0.120
10/28 2	140	1	50	122	60	2	2.75	0.124	0.25	0.132	0.107
10/28 3	140	-	200	488	60	3.4	3.9	0.233	6.5	0.132	0.120
10/28 4	140	1	200	488	60	3.4	3.84	0.242	8	0.132	0.120
10/28 5	~ 450	-	50	122	60	2	2.65	0.099	0.2	0.120	0.09
10/28 6	~ 450	-	200	488	60	3.4	3.92	0.216	3.75	0.120	0.09
(full size Ag electrodes)											
11/4 1	~ 450	1	100	244	60	3.6	4.12	0.317	0.8	0.230	0.102
11/4 2	~ 450	1	100	244	60	3.3	4.1	0.228	0.9	0.150	0.102
11/4 3	~ 450	1	200	488	60	4.4	4.92	0.326	1.5	0.212	0.102
11/4 4	~ 450	1	200	488	60	4.4	4.9	0.343	0.6	0.172	0.102
11/4 5	~ 450	-	* dipped in acetate only					0.474	3.7	0.180	0.102
11/4 6	~ 450	-	* dipped in acetate only					0.764	5.8	0.173	0.093

(full size Ag electrodes)