



The electrolytic synthesis of battery active manganese dioxide  
by Edward F Sylvain

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree  
of Master of Science in Electrical Engineering

Montana State University

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Abstract:

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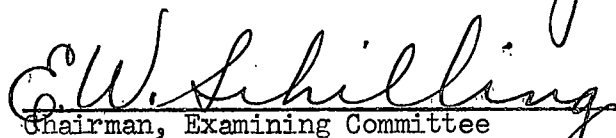
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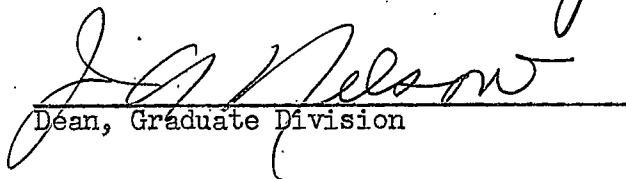
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Montana State College

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Head, Major Department

  
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TABLE OF CONTENTS

	Page
ABSTRACT. . . . .	4
I Introduction. . . . .	5
II Experimental Work . . . . .	8
A. Apparatus . . . . .	8
1. Power Supply. . . . .	8
2. Electrolyte Container and External Heat Supply	10
3. Electrolyte and Electrode Supports. . . . .	11
4. Drying Oven . . . . .	12
B. Procedure . . . . .	13
1. Preparation of the Electrolyte. . . . .	13
2. Electrolysis. . . . .	13
3. Anode Stripping . . . . .	14
C. Observations and Results. . . . .	16
1. Electrode Stability . . . . .	16
a. Anodes. . . . .	17
b. Cathode . . . . .	18
2. Cell Voltages . . . . .	19
a. Anode Current Density . . . . .	19
b. Electrolyte Acidity . . . . .	19
c. Electrolyte Manganese Sulphate Concentra-	20
tions . . . . .	20
d. Anode to Cathode Spacing. . . . .	20
3. Current Efficiencies and Kw-Hr Per Pound of	20
MnO <sub>2</sub> . . . . .	20
a. Anode Current Density . . . . .	23
b. Electrolyte Acidity . . . . .	25
c. Cell Temperature. . . . .	25
d. Anode Material. . . . .	26
e. Electrolyte Manganese Sulphate Concentra-	27
tions . . . . .	27
f. Anode to Cathode Spacing. . . . .	27
4. Electrolytic MnO <sub>2</sub> Data. . . . .	28
5. Analysis of Electrolytic MnO <sub>2</sub> . . . . .	29
6. Results of Battery Performance Tests. . . . .	29
III Commercial Applicability of Electrical Load	
Characteristics. . . . .	30
A. Current Density . . . . .	30

	B. Electrolyte Concentrations. . . . .	34
	C. Power Failure. . . . .	35
	D. Electrode Spacing and Cell Size . . . . .	36
IV	Conclusions. . . . .	37
V	Literature Cited . . . . .	38
VI	Appendix. . . . .	39
	Table I Electrolytic MnO <sub>2</sub> Data. . . . .	40
	Table II Analysis of Electrolytic MnO <sub>2</sub> . . . . .	46
	Table III Battery Test Data . . . . .	47
	Figure 2 The Relation of Current Efficiency, Energy Requirements and Cell Voltage to Various Current Densities . . . . .	48
	Figure 3 The Relation of Current Efficiency, Energy Requirements, and Cell Voltage to Various Electrolyte Acid Concentrations . . . . .	49
	Figure 4 The Relation of Current Efficiency and Energy Requirements to Various Manganese Sulphate Concentrations. . . . .	50
	Figure 5 The Relation of Current Efficiency, Energy Requirements, and Cell Voltage to Electrode Spacing. . . . .	51

ABSTRACT

The experimental work concerning the electrode stability, current efficiencies, and power requirement per unit weight of manganese dioxide has been undertaken to establish the type of electrical load to be expected in the electrolytic production of battery active manganese dioxide from Montana manganese bearing ores. The results have been considered not only to the applicability of the electrical load to a commercial process but also as to the quality of the product.

## I INTRODUCTION

The successful production of battery active manganese dioxide is a matter of considerable importance for both military and commercial utilization. In war times, especially during the last world war, there was a heavy demand for a manganese dioxide that would be pure enough to act as a depolarizer in dry cell batteries. In the past, this demand has been met by natural ore supplies mainly from the African Gold Coast. In the future, it is evident from the results of this thesis and other treatises concerning manganese dioxide production that the demand will be met by an electrolytic manganese dioxide. Obviously this will be a bonus to American industry.

Since the chief source of natural ore available to the United States is the African Gold Coast ore, the production of electrolytic manganese dioxide from local ore supplies has a twofold effect: (1) should the natural ore supply be cut off, national security will not be jeopardized by lack of battery active manganese dioxide; (2) an abundant supply of ore heretofore not used for batteries (rhodochrosite), can now be utilized in the electrolytic process to yield a battery active manganese dioxide with better characteristics than natural ores under heavy current drain conditions.

Russian pyrolusite, previous to 1914, was a standard depolarizer used in dry cells. The supply was cut off due to World War I, and native pyrolusites were tried with poor results. These results led experimenters to believe that something more than the manganese dioxide content determined

the action in the cells, since native pyrolusite with as much as ninety-five per cent manganese dioxide was tried as a substitute for Russian pyrolusite. Electroplating of manganese dioxide has been in the experimental stage since as early as 1918, however, at that time the importance of the crystal structure of the manganese dioxide was not recognized. Later work done by G. W. Nichols (1) in 1932, brought to light some of the problems involved in the production of electrolytic manganese dioxide; namely the dependence of the electroplating on the microscopic surface of the anode. One year later, Dr. Peter Marx (2) published a paper at Bitterfeld, Germany which did little more than confirm American conclusions on the matter.

It wasn't until World War II that, with the increased research due to the shortage of natural manganese dioxide ore, the importance of the crystal structure became apparent. The type of crystal structure found to be most satisfactory for use in dry cell batteries is called "gamma structure" or, more commonly, "gamma phase". Recently, in 1949, Georgia Institute of Technology (3) did a considerable amount of work, under the auspices of the United States Army Signal Corps, which is discussed in detail in their report titled "The Electrolytic Synthesis of Battery Active Manganese Dioxide". The Georgia Institute of Technology results were a positive indication that the electrolytic manganese dioxide could be produced under certain process conditions to yield gamma phase manganese dioxide. Also, work concerning the anode problem was conducted at Georgia Institute of Technology.

Further research on the project, under the auspices of the United

States Army Signal Corps, is being carried on by the Montana State College Engineering Experiment Station at Bozeman, Montana. Since Montana is the leading producer of manganese ores, Montana ores such as rhodochrosite from Butte and pyrolusite from Phillipsburg are used in the research work.

Since the process of producing battery active manganese dioxide is of an electrochemical nature, the research is conducted as a joint project between the Electrical Engineering and the Chemical Engineering Departments of Montana State College. Consequently, two theses will be written on the subject at this time. This thesis will cover the electrical aspects of the research, and a second thesis by Arthur M. Magnuson will incorporate the chemical engineering aspects.

Battery performance tests on two electrolytic manganese dioxide samples from runs Carbon 7 and Carbon 22 are being conducted by the Squier Signal Laboratories. The results of the initial battery test are included in this thesis. Further results from the Squier Signal Laboratories will be attached to this thesis when available. Chemical analyses on electrolytic manganese dioxide were conducted by the United States Army Signal Corps Laboratories on numerous samples.



## II EXPERIMENTAL WORK

The following discussion of experimental work pertaining to the "APPARATUS" and "PROCEDURE" will be incomplete because the discussion of the apparatus used in preparing the electrolyte and the preparation of the electrolyte itself will be explained in detail in the chemical engineering thesis. In this thesis mention of the chemical engineering techniques used will be only qualitative when clarity necessitates.

### A. APPARATUS

The basic equipment used in the research work, after the electrolyte is prepared, are a suitable d-c power supply, method of heating the electrolyte during operation, electrode and electrode supports, and a drying oven to determine the dry weight of anodes before and after operation.

#### 1. Power Supply

Run Carbon 1 power supply was a 33 volt, 125 ampere d-c generator which is still available in the electrical engineering laboratory in the event that a greater power supply should be needed. A d-c generator with a capacity of 50 volts and 15 amperes was used in all runs except Carbon 1. To excite the field of this d-c generator, a "free wheeling" rectifier circuit was designed. The rectifier provided a convenient means of controlling the output of the generator since the controlling variac of the rectifier was placed directly on the cell table. The capacity of the d-c generator was found to be quite satisfactory for the laboratory work because, by proper design of the anodes, it was possible to obtain current densities up to 40 amperes per square foot. Indeed, the current densities

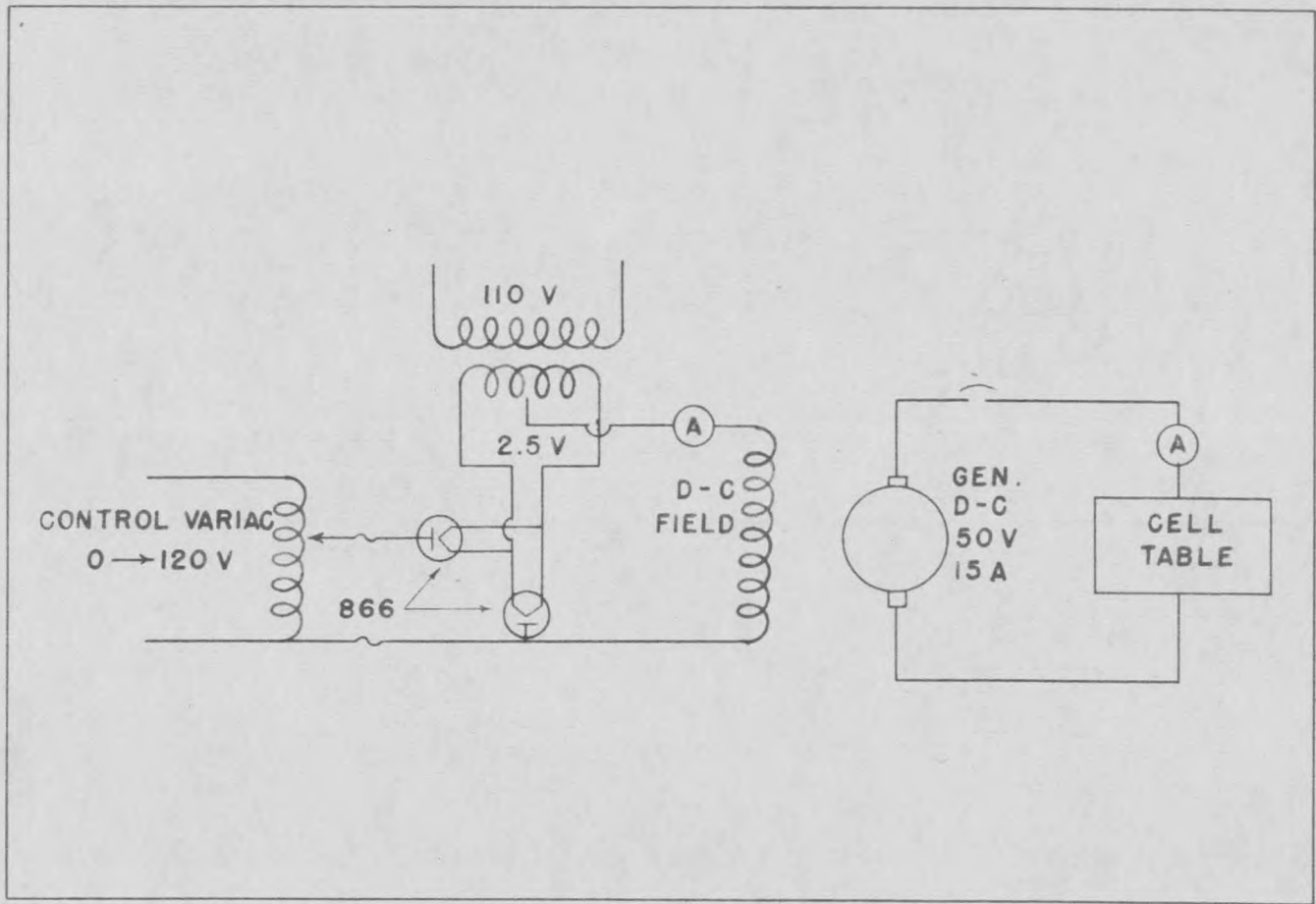


Figure 1 - Schematic Diagram of the Electrical Apparatus Used in the Electrolysis

obtained covered more than the practical range of the process as will be discussed subsequently. In passing, it might be mentioned that the ripple in the output voltage of the d-c generator caused by the field rectifier, as shown on an oscillograph, was approximately equal in magnitude to the inherent ripple caused by the commutator of the d-c generator. Thus, a low ripple factor voltage was maintained for the electrolysis. The electrical set up is shown diagrammatically in Figure 1.

## 2. Electrolytic Container and External Heat Supply

In order to maintain the electrolyte at about  $93^{\circ}$  C. during experimental runs, it was necessary to heat the cells by an external means. This was accomplished by using a hot plate of 550 watts capacity underneath each electrolyte container. Consequently, the electrolyte container was made of pyrex with dimensions as follows: 6 inch diameter by 11  $\frac{3}{4}$  inch height with approximately 3900 cubic centimeters useable volume. With this arrangement, heat could be applied directly to the cell and controlled by two methods. One control was by means of the low-medium-high switch on the hot plate, and the other control was through variacs to which the hot plates were electrically connected. With the pyrex container placed directly on the hot plate, the unit was placed on a cell table. Attached to the table was a cell rack which served as a terminal board for electrical connections and also prevented the pyrex container from any horizontal movement which would cause the container to slip from the hot plate.

### 3. Electrodes and Electrode Supports

In all the experimental runs one type of electrode holder was used. The electrode holder was made from a 1/4 inch sheet of polystyrene which is resistant to sulphuric acid. The outside dimensions of the polystyrene holder are 4 inches by 8 inches with slots provided for the placement of the anode, cathode, and a thermometer. To prevent slipping through the slots, the anode, cathode and thermometer in each electrode holder were clamped in place. With electrodes and thermometer clamped to the electrode holder, the unit was placed directly on the pyrex container in such a manner that the anode, cathode, and thermometer extended into the electrolyte. The electrode holder rested on the top rim of the pyrex container. It was then a simple matter to make electrical connections to the terminal board.

In all the experimental runs, the cathode was made from a chemical lead sheet 1/16 inches thick with dimensions such that the cathode area was approximately twice the anode area. To insure plating on both sides of the anode, a cathode was placed on each side of the anode; the total cathode area being twice the anode area.

Available for research were two types of anodes. The first anode used, in runs Carbon 1 through Carbon 6, was a hard carbon rod, 7/8 inch in diameter. It is believed that this particular type of anode was used in "arc lights". At any rate, the anodes of this type proved of no importance since they did not provide satisfactory results. The second type of anode used was an "Acheson Graphite" of grade A.G.R. as designated

by the National Carbon Company. This type of anode was used in all runs subsequent to Carbon 6. The dimensions of the anode used in most runs was 9 inches by 4 inches by 1/2 inch. In some runs it was necessary to design the anodes with a smaller effective area (area submerged in the electrolyte) in order to achieve high current densities. To find the effective area, in all cases, the actual current divided by the current density will give the effective area. (See Table I for data). Acheson Graphite of grade A. G. R. is a much softer material than the first carbon rod used. This soft material did lend itself to more satisfactory results.

#### 4. Drying Oven

It was found convenient to use a drying oven to determine the dry weights of the anodes before and after an experimental run. In general, the graphite absorbs about 10 grams of the electrolyte. In order to determine current efficiencies, the dry weight of the anode was recorded before a run; and at the end of the run, the anode plus manganese dioxide was dried in the oven at a temperature of about 80-85<sup>o</sup> C., and the weight recorded. By subtracting the dry weight of the anode before a run from the dry weight of the anode following the run, the manganese dioxide deposit was determined.

## B. PROCEDURE

The procedure followed in producing battery active manganese dioxide from manganese bearing ore can be summarized in three steps: (1) Preparation of the Electrolyte. (2) The Electrolysis. (3) Anode Stripping.

### 1. Preparation of the Electrolyte

Briefly, it was required that the manganese bearing ore be put into a manganese sulphate solution with certain concentrations of manganese. In the process of obtaining the manganese sulphate, sulphuric acid was employed. The final solution containing manganese sulphate and sulphuric acid constituted the electrolyte. The elimination of impurities and the actual preparation of the electrolyte for various conditions is discussed in detail in the chemical engineering thesis on this research.

### 2. Electrolysis

The electrolysis itself was performed by passing a prescribed amount of current through the electrolyte by means of the electrodes. However, certain chronological steps must be taken in the electrolysis process. With pyrex containers filled to a prescribed volume of electrolyte, the hot plates were turned on allowing the electrolyte to attain a temperature of about  $93^{\circ}$  C. This took approximately 2 hours. When the electrolyte reached  $93^{\circ}$  C. the cell holder, complete with anode, cathode, and thermometer was placed in the cell and connected electrically to the d-c generator. Before starting the generator, it was necessary to allow about 2 minutes for the electronic tubes in the rectifier circuit to warm up. After starting the generator, the control variac in the rectifier circuit was varied until the ammeter indicated an appointed

amount of current passing through the cells.

While electrolysis was taking place, it was necessary to replace the spent electrolyte periodically with fresh solution of neutral manganese sulphate. At the same time, the sulphuric acid generated was withdrawn in proper amounts. The amount of fresh solution added and the amount of acid removed is covered in detail in the chemical engineering thesis. During the experimental runs, the changing of solution was performed every 1/2 hour or every hour depending on the quantity added and removed. It has been the practice in the research during the past year to average the voltage and current reading for the period between replenishment of the spent electrolyte.

When stopping a run the control variac was changed until the ammeter reading was zero. When the ammeter read zero, it was then safe to disconnect the cells and remove the electrodes from the electrolyte.

### 3. Anode Stripping

The method used in the past by other experimenters to remove the manganese dioxide from the anode was simply by scraping the anode with a wood chisel. This was a most unsatisfactory operation, because the adherence of the manganese dioxide to the graphite anode is of such strength that removal of the manganese dioxide without graphite content was practically impossible. Also, this was a rather tedious process. It was found, during this research, that if the anodes were boiled in the electrolyte while still in the electrode holder with the cathodes, the manganese dioxide, after a matter of 4 to 5 hours time, became loose at the surface of the anodes. This was due to the softening of the anodes.

However, the softening occurs on the surface of the anodes only, and does not prevent further use of the anodes. Since carbon is mixed with manganese dioxide in preparation for dry cell batteries, the carbon impurity was not considered detrimental. In fact, A.G.R. graphite has been found to be superior for dry cell battery use.



### C. OBSERVATIONS AND RESULTS

In order to determine the type of electrical load involved in the production of battery active manganese dioxide from local ores, it was necessary to establish the range of practical operating conditions. A series of runs, designated Carbon 1 through Carbon 21, were performed for that purpose. The essential data has been placed on curves and tables which shall be referred to throughout the following discussion. Whenever possible, theoretical consideration will be given along with the discussion. That is, some of the phenomena in this electrolytic process was not fully understood. For instance, why, when under the same conditions and when both anodes are good electrical conductors, does one anode material lend itself to the process very well, while another will not. Another phenomenon is the fact that electrolytic manganese dioxide is not a conductor of electricity when produced at cell voltage over 1.7 volts (4); and yet, a current was passed through the cells with about the same voltage required with and without a manganese dioxide plating on the anode. Does this mean that, as G.W. Nichols concluded, the plating could only take place underneath the manganese dioxide coating? (2). For the purpose of establishing the characteristics of the electrical load, the understanding of such action is of secondary importance in this thesis.

#### 1. Electrode Stability

Much more work has been done on the problem of finding a suitable

anode than is presented here. However, to show the effects of different types of anode material on the electrolytic process, both types of anodes used in this research will be discussed, although the results with the hard carbon rod anode were far inferior to the A.G.R. graphite anode results. A more complete list of anodes tried will be found in the references, mainly in the Georgia Institute of Technology (3) report and the publication by Dr. Peter Marx (2).

It is interesting to note that Storey, Steinhoff and Hoff (4) found that if for graphite anodes the potential drop across the cell was kept below the decomposition potential of water acidified with sulphuric acid (approximately 1.7 volts), there would be no deterioration of the anodes. However, this is impractical for a commercial operation.

a. Anodes

The chief factor affecting the anodes is current density. For the hard carbon anodes, current densities of 45-60 amps./ft.<sup>2</sup> caused so much deterioration to the anodes that the electrolyte became opaque from suspended carbon after as little as 3 hours of run time. The A.G.R. graphite anodes did not undergo deterioration to such a degree. When A.G.R. graphite anodes were used with 39 amps/ft.<sup>2</sup> current density and 5 hours of run time, the electrolyte was almost totally clear of suspended carbon. The deterioration at this current density seemed slight, as only a small amount of carbon was found on the bottom of the electrolyte container. This amount was an estimated 1/2 gram or less.

Although Van Arsdale and Maier (5) did not mention any anode deterioration for current densities up to 30 amps./ft.<sup>2</sup> using A.G.R. graphite anodes, the Georgia Institute of Technology (3) did find considerable damage to A.G.R. graphite anodes after long periods of operation (50-75 hours at current densities of above 20 amps./ft.<sup>2</sup>).

The acid concentration caused some anode deterioration, but not to such an extent as did the current density. In run Carbon 15, Cell 3 a discoloration of the electrolyte was noticed after about 10 hours of operation. The amount of suspended carbon was still not enough to cause concern after 15 hours of operation.

Temperature seemed to be the cause of serious anode deterioration. For run Carbon 6, Cells 1, 2, 3, and 4, the decreased temperatures caused much anode deterioration with other factors remaining constant. In fact, at 40° C. cell temperature the anode was attacked to such a degree that large surfaces of the hard carbon rod anode were demolished. Under the same conditions, at a temperature of 92° C., the anode did not undergo such intense destruction. Since it is not advisable to operate at low temperatures (see "Anode Current Efficiencies and Kw-Hr per Pound MnO<sub>2</sub>:" "Cell Temperatures.") this detrimental action may be eliminated.

b. Cathode

In all the experimental runs chemical lead was used as the cathode. The chemical lead resisted sulphuric acid reaction, and was not

affected by the current density. In the electrolytic process the chemical lead cathode acted as a 100 per cent liberator of hydrogen.

## 2. Cell Voltages

During the experimental runs the average voltage per cell was obtained and plotted along with the curves of current efficiencies and kw-hr per pound  $MnO_2$ . The voltages were obtained directly from the anodes to eliminate terminal contact potential drop and IR drop through the electrical connection associated with the cells. Also, the voltages per cell were averaged over an entire run. It was found that after stopping the electrolysis, a back voltage of about 1.5 volts existed for a short duration (about 5 minutes) and then dropped to a value of about 0.7 volts.

### a. Anode Current Density

An increased average voltage per cell was experienced with an increase in current density. The voltage increase is approximately linear in the range of from 1.58 volts at a current density of 3.37 amps./ft.<sup>2</sup> to 2.56 volts at 39 amps./ft.<sup>2</sup> with the graphite anodes. This is indicated in Figure 2.

### b. Electrolyte Acidity

Within the useful range of acidity, there was no variation in the average voltage per cell; other factors held constant. A slight voltage increase occurred for acidities between 33.5 and 67 gm./l.  $H_2SO_4$ . The value of the voltage at 67 gm./l. was found to be 1.9 volts; and

at 33.5 gm./l. the value of the voltage was 2.0 volts. Both values were taken from runs where the current density was 10 amps./ft.<sup>2</sup>, as shown in Figure 3.

c. Electrolyte Manganese Sulphate Concentrations

The average voltage per cell was not affected by a change in manganese sulphate concentration. For the entire range of manganese concentrations plotted in Figure 4, i.e., 100 to 176 gm./l. MnSO<sub>4</sub>, the voltage was 1.875 ± 0.025 volts under the conditions given in Figure 4.

d. Anode to Cathode Spacing

As would be expected, an increase in the spacing of the electrodes caused a greater voltage drop across the cell with all other factors being held constant. This voltage drop was due to the longer current path through the electrolyte. The average voltage drop occurring at a spacing of 0.438 inch was 1.71 volts, and at a spacing of 1.75 inches the voltage drop was 1.92 volts. This is indicated in Figure 5.

3. Current Efficiencies and Kw-Hr per Pound of MnO<sub>2</sub>

The anode current efficiency is the ratio of the actual amount of MnO<sub>2</sub> plated on the anode to the amount that should be plated on according to Faraday's second law of electrolysis, if all the manganese combined with oxygen to form MnO<sub>2</sub>. To explain this further, consider the chemical action in the cell:  $\text{MnSO}_4 + 2 \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{H}_2 + \text{MnO}_2$ . The manganese changes valence from two, in MnSO<sub>4</sub> to four, in MnO<sub>2</sub>, or a total change of

valence of two. The hydrogen is given off at the cathode, and the  $MnO_2$  is, of course, plated on the anode. Now then, Faraday's law states that the weight of a metal deposited, or of a gas set free by an electrolytic process is directly proportional to the gram-equivalent weight of the metal or gas; and that 96540 coulombs will deposit metal or set off gas to the amount of one gram-equivalent weight. In equation form the law is as follows:

$$m = \frac{qw}{96540 n}$$

where m is the weight in grams of the metal deposited, or of the gas set free.

q is the quantity of electricity in coulombs passing through the electrolyte.

w is the atomic weight of the material deposited, or set free.

n is the valence of the material.

Using a valence change of two and the atomic weight of Mn as 54.93, and the atomic weight of  $O_2$  as 32, the theoretical deposit of  $MnO_2$  is, according to Faraday's Law:

$$m = \frac{q \times 86.93}{96540 \times 2} \text{ Gm. } MnO_2$$

and q = hours x 3600 x amperes

$$\text{therefore, } m = \frac{\text{hours} \times 3600 \times \text{amperes} \times 86.93}{96540 \times 2}$$

$$m = (1.62 \times \text{amperes} \times \text{hours}) \text{ Gm. } MnO_2$$

and, finally, the current efficiency is:

$$\text{current efficiency} = \frac{\text{actual weight of MnO}_2 \text{ deposited in grams} \times 100}{1.62 \times \text{amperes} \times \text{hours}}$$

Directly related to the current efficiencies is the Kw-Hr per pound of MnO<sub>2</sub>. To show the method used in calculating this from the data given on Table I, a specific example, run Carbon 12 from Table I, will be taken as follows:

Average volts per cell . . . . . 1.80  
Grams MnO<sub>2</sub> produced. . . . . 60.5  
Actual current. . . . . 3.75  
Hours of run. . . . . 17.25

$$\text{Kw-Hr} = \frac{1.80 \times 3.72 \times 17.25}{1000}$$

$$\text{Pounds MnO}_2 = \frac{60.6}{454}$$

$$\text{Kw-Hr per pound MnO}_2 = \frac{1.80 \times 3.72 \times 17.25 \times 454}{60.5 \times 1000} = 0.865$$

It should be mentioned that since the average voltage per cell was taken directly from the anodes, the power requirements for a commercial process would be slightly greater depending on the terminal voltage drop and IR voltage drop through the associated electrical connections. In the case of both current efficiencies and Kw-Hr per pound MnO<sub>2</sub> the values given in Table I are uncorrected for impurities. The error introduced in current efficiencies and Kw-Hr per pound MnO<sub>2</sub> would not be serious since the impurities constitute a small percentage of the anodic deposit.

It is interesting to note that according to Kameyama and Iida

(metallborse 1932, p. 1183) it is possible, by use of alternating current, to obtain a dry cell  $MnO_2$  if the  $MnSO_4$  is decomposed at the higher temperatures. This was tried by Peter Marx (2) with platinum gauze electrodes having an electrode surface of  $2 \text{ cm.}^2$ . The only result given was that with a current density of  $50 \text{ amp./dm.}^2$  (about  $463 \text{ amps/ft.}^2$ ) and a voltage of about 20-25 volts, the power consumption was unreasonably high in comparison to the use of direct current.

a. Anode Current Density

The data obtained for the variation of current density with electrolyte concentrations of  $67 \text{ gm./l. H}_2\text{SO}_4$  and  $137.5 \text{ gm./l. MnSO}_4$ , electrode spacing of 1 inch, temperature of  $93^\circ \text{ C.}$ , has been plotted in Figure 2. Examination of the curve of current efficiencies indicates a maximum efficiency of about 63.7 per cent, occurring at a current density of  $6.72 \text{ amps/ft.}^2$ . The energy required to produce a pound of  $MnO_2$  at this current density is  $0.684 \text{ Kw-Hr per pound MnO}_2$ . At lower current densities, below  $5 \text{ amps./ft.}^2$ , the current efficiencies drop rapidly, and the energy requirement increases so rapidly that this might well be called the cutoff point of the electrolysis for all practical purposes. For current densities above  $6.72 \text{ amps./ft.}^2$  the current efficiencies and Kw-Hr per pound  $MnO_2$  have a more gradual increase and decrease respectively, up to a current density of about  $20 \text{ amps./ft.}^2$ . Beyond this point, the electrolysis becomes impractical for two reasons: (1) the energy requirement becomes excessively high (about  $2.3 \text{ Kw-Hr}$  for current density of



39 amps./ft.<sup>2</sup>) (2). The anode deterioration, not evident by inspection of the curves, becomes excessive.

Although the amount of anode deterioration is rather difficult to predict, the amount of anode deterioration found after 5 hours run time at 39 amps./ft.<sup>2</sup> current density was an estimated 1/2 gram found on the bottom of the cell. This deterioration occurred when graphite anodes were used. With the hard carbon rod anodes, the deterioration at current densities of 45-60 amps./ft.<sup>2</sup> was such that after about 10 hours of operation these anodes lost considerable weight.

In general, there is a limit to the current densities useable for reasonable current densities and power requirements. The lower limit is due to the cutoff point of the electrolysis, and the upper limit is dependent on the type of anode used.

Since the current efficiencies are governed by the amp-hr of electrolysis the only essential difference between current efficiencies and energy required to produce a pound of MnO<sub>2</sub> is in the voltage per cell, the Kw-Hr per pound MnO<sub>2</sub> curves follow an inverse relationship with current efficiencies. As discussed under "Cell Voltages," the amount of voltage variation is small for most cases, and as a result of this, the linearity of the inverse relationship is evident from Figures 2, 3, and 4.

b. Electrolyte Acidity

As in the case of current densities, the electrolyte acidity effects the current efficiencies and energy required in a similar manner. That is, there is a cutoff point, and a point for maximum values of current efficiencies. As shown in Figure 3, with an acidity of about 95 gm./l.  $H_2SO_4$  and the following conditions: 137.5 gm./l.  $MnSO_4$ , 10 amps./ft.<sup>2</sup>, 1 inch electrode spacing, graphite anodes of A.G.R. type; the maximum current efficiency is about 72 per cent, and the energy required to produce a pound of  $MnO_2$  is found to be 0.741 Kw-Hr. The cutoff point due to the electrolyte acidity is in the region below 10 gm./l.  $H_2SO_4$  for the same conditions as stated above. The upper limit of acidity is not definitely established; it is believed that the anode deterioration, as in the case of current densities, will be the determining factor. This is based on the literature consulted (4).

c. Cell Temperature

A run called "Carbon 6" was made to determine the effect of cell temperatures on current efficiencies and power requirements. Although this run was made with the hard carbon rod anodes, where at best only 26 per cent efficiencies were obtained, it demonstrates the fact that the process should be conducted with a high temperature. On run Carbon 6 not only did the current efficiencies decrease with lower temperatures, but also the anode deterioration

was more severe at the lower temperatures. For instance, Van Arsdale and Maier (5) stated that a higher temperature will increase the speed of hydrolysis so that the manganic solutions do not have time to diffuse away from the electrode before being decomposed; and that the rapid breaking up of manganic salts prevents further oxidation resulting in oxygen formed. In addition to this, Georgia Institute of Technology (3) found that from the numerous samples sent in to the Army Signal Corps Laboratories, runs conducted above 80° C. produced MnO<sub>2</sub> that was practically all gamma phase. Lower temperatures gave a mixture of gamma phase MnO<sub>2</sub> and cryptomelane. With these results in mind, all runs from Carbon 7 through Carbon 22 were conducted at 93° C. ± 3° C.

d. Anode Material

Although only two types of anodes were used in the electrolysis to date here at Montana State College, the current efficiencies and energy requirements demonstrate the dependence of efficient electrolysis on the type of anode used. For example, run Carbon 1 using a hard carbon anode at 15 amps./ft.<sup>2</sup>, 137.5 gms./l. MnSO<sub>4</sub>, 67 gms./l. H<sub>2</sub>SO<sub>4</sub>, 91° C., had a current efficiency of 23 per cent, and energy required was 2.43 Kw-Hr per pound MnO<sub>2</sub>; while run Carbon 18, Cell 2 using A.G.R. graphite anode at 18.6 amps./ft.<sup>2</sup>, 137.5 gms./l. MnSO<sub>4</sub>, 67 gms./l. H<sub>2</sub>SO<sub>4</sub>, 93° C., had a current efficiency of 54 per cent, and the energy requirement was 0.906 Kw-Hr per pound MnO<sub>2</sub>. Accord-

ing to the chemical equation of the electrolysis, it would appear as if either anode would prove satisfactory, i.e., since the prime reason for the anode is to provide a path for the current through the cells, and both types of anodes are good conductors of electricity, the electrolysis should not be effected by the type of electrical conductor used. Because there is a great difference in the results of the two types of anodes used; it would seem logical to attribute this inconsistency to the microscopic surfaces of the anodes.

e. Electrolyte Manganese Sulphate Concentration

With a current density of 10 amps./ft.<sup>2</sup>, electrolyte acidity of 67 gms./l. H<sub>2</sub>SO<sub>4</sub>, 93° C., it was found that a maximum current efficiency of 73.4 per cent existed with a energy requirement of 0.735 Kw-Hr per pound MnO<sub>2</sub>, for MnSO<sub>4</sub> concentration of 150 gm./l. Although the current efficiencies varied from 43 per cent to 73.4 per cent, the Kw-Hr per pound MnO<sub>2</sub> varied from 1.23 to 0.735, and for the most part remained in the neighborhood of about 0.9 Kw-Hr per pound MnO<sub>2</sub>. This is shown in Figure 4.

f. Anode to Cathode Spacing

It was found that increased spacing from cathode to anode gave a slightly increased current efficiency (from 52 per cent at 0.438 inches to 58.8 per cent at 1.75 inches.) Because of the increased voltage per cell, the energy requirement did not change for the spacing of 0.438 inches to 1.75 inches, but remained at 0.90 Kw-Hr per

pound  $MnO_2$ . It would seem that for the same energy requirement a larger spacing of electrodes should be used to utilize the increased current efficiency; however, if the greater amount of cell space is considered on a large scale operation, the advantage of increased current efficiencies might be over balanced by the cost of floor space. Figure 5 shows the relation of current efficiencies and power requirements with electrode spacings of 0.438 inches, 1 inch and 1.75 inches.

If time would have permitted, it would have been interesting to experiment on electrode spacings less than 0.438 inches apart. Since electrolytic  $MnO_2$  is not a conductor of electricity, once a plating was on the anode, there would be no danger of short-circuiting the anode and cathode.

#### 4. Electrolytic $MnO_2$ Data

Reference has already been made to Table I and the associated curves. Table I has been prepared directly from the notebook used during the research. The numeral superscripts refer to notes which are listed on the page immediately following Table I. The curves given in Figures 2, 3, 4, and 5 were constructed directly from the data given in Table I. Table I and graphs are included on pages 40 to 51.

#### 5. Analysis of Electrolytic $MnO_2$

The chemical analysis was made on certain samples by the Fort Monmouth Laboratories. The results of these analyses have been compiled in Table II. In all cases where a chemical analysis was made the structure

of  $MnO_2$  was found to be "gamma phase". Run Carbon 12 sample was superior to the other samples analyzed. This is shown in Table II.

#### 6. Results of Battery Performance Tests

Battery performance tests were performed on a sample from run Carbon 7 by the Battery Branch of the Squier Signal Laboratories. The result of the initial test is given in Table III. Also, a run to be called "Carbon 22" will henceforth be completed to provide a battery test. The run will be made under the same conditions as existed for Carbon 21. Provision will be made to include such data in this thesis when obtainable under Table III.

It should be noted that the ore from the African Gold Coast, when made up into a battery and tested gives an Average Initial Service of about 85 hours when discharged through  $166 \frac{2}{3}$  ohms; while Carbon 7 sample when undergoing a battery test discharge through  $166 \frac{2}{3}$  ohms gives an Average Initial Service of 109.4 hours, as shown in Table III. This manifests the superiority in this respect of run Carbon 7 sample to the African ore. The shelf life of the battery made from the sample of run Carbon 7 may or may not compare to that of the battery made from African ore. Subsequent tests by the Squier Signal Laboratories will determine the shelf life of the battery made from run Carbon 7 sample.

### III COMMERCIAL APPLICABILITY OF ELECTRICAL LOAD CHARACTERISTICS

In cases where electric energy rates are based on a peak demand of electrical load, and where it is desirable to have a high load factor, electrolytic  $MnO_2$  offers attractive commercial possibilities. Also, in many cases there is seasonal power available that could very well be utilized in the electrolytic production of battery active  $MnO_2$  without redesign of the electrolysis apparatus. From the experimental data the only seriously undesirable factor is the lack of a suitable anode. Although graphite anodes can be used up to a current density of about 20 amps./ft.<sup>2</sup>, it would be expedient to have an anode that would not deteriorate under high current densities so that the time involved in the electrolytic production of battery active  $MnO_2$  could be most efficiently utilized.

#### A. Current Density

In order to have a load that would be applicable for obtaining a high electrical load factor and reduced power rates on a peak demand basis, the electrical load would have to be rather flexible. To illustrate what is meant by the flexibility of the electrolytic load in producing battery active  $MnO_2$ , a specific example will be given. In the example, it will be assumed that a cell room for the electrolysis is to be used having the following design:

Anode. . . . . A.G.R. graphite with effective area of 15 ft.<sup>2</sup>  
Cathodes . . . . . Chemical lead with effective area of 15 ft.<sup>2</sup>  
Electrolyte. . . . Concentrations of 67 gm/l.  $H_2SO_4$  and 137.5 gm/l.  
 $MnSO_4$   
Temperature. . . . . 93° C.

Electrode spacing. . . . . 1 inch  
 Cell unit. . . . . 20 anodes and 21 cathodes  
 Number of cell units. . . . . 14  
 Contact potential. . . . . Assumed to be 0.30 volts

In a 24 hour period, the expected output of MnO<sub>2</sub>, power required, and time to obtain a ton of MnO<sub>2</sub> based on the experimental data found on the curves of Figure 2, with a current density of 10 amps./ft.<sup>2</sup> would be:

$$\frac{(10 \times 15) \frac{\text{amps}}{\text{anodes}} \times \frac{1.62 \text{ gm MnO}_2}{\text{amp-hr}} \times 24 \text{ hr.} \times 14 \text{ cell units} \times \frac{20 \text{ anodes}}{\text{cell unit}}}{454 \text{ gm./lb.}} =$$

2050 lb. MnO<sub>2</sub> in 24 hours.

The power required would be:

$$\frac{2050 \text{ lb.}}{\text{lb. MnO}_2} \times \frac{0.906 \text{ Kw-Hr}}{\text{lb. MnO}_2} \times \frac{2.18}{1.88} = 2160 \text{ Kw-Hr for a 24 hr. period.}$$

where the quantity  $\frac{2.18}{1.88}$  allows for additional power due to contact voltage drop.

The time required to produce a ton of MnO<sub>2</sub> would be:

$$\frac{2000}{2050} \times 24 = 23.4 \text{ hours.}$$

The cost of energy at 1/4 cent per Kw-Hr is \$5.27 per ton. Since AGR graphite anodes are being used, a safe variation in the current density would be from 5 amps./ft.<sup>2</sup> to 18.6 amps./ft.<sup>2</sup>. To show the effect of variation of current density the values used above will be taken as a base for per unit values, i.e., 10 amps./ft.<sup>2</sup> corresponds to a per unit current density of 1.0; and so on for the other values above. Since the



extreme conditions of flexibility are the values of interest, Table IV is shown below:

TABLE IV. Flexibility of Output and Electrical Load in Per Unit Values

Current Density	Output of MnO <sub>2</sub> in 24 hr.	Energy Required For Output of MnO <sub>2</sub>	Time Required for ton of MnO <sub>2</sub>	Cost of Electrical Energy Per Ton of MnO <sub>2</sub>
1	1	1	1	1
0.5	0.444	0.477	2.25	1.07
1.86	1.765	2.14	0.445	1.21

Inspection of Table IV indicates that the load (energy required for output of MnO<sub>2</sub>) may be varied from a per unit energy requirement of 0.477 to 2.14 with a variation of cost of electrical power per ton MnO<sub>2</sub> in per unit values of only 1.07 to 1.21. In other words, the electrical load can be varied through a wide range without increasing to any appreciable amount the power cost of the electrolysis for a unit weight of MnO<sub>2</sub>. This would be an important item, if on a large scale operation the electricity cost per month was based on a peak demand for that month. That is, at the time of anticipated peak demand, the electrolysis power requirement could be reduced and thus save a considerable amount of power cost for the month. Conversely, the production could be increased when a slack period of power demand occurred and thus the load factor of an electrolysis plant could be maintained at a higher value than if this practice were not adopted.

The actual values involved may be found by multiplying the per











































