Chemical synthesis of battery-active manganese dioxide
by Robert L Nickelson

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
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and to determine which syntheses might be adapted to commercial production of battery-active
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syntheses. These samples were given a chemical analysis consisting of determination of total
manganese, available oxygen, moisture content, and pH, The physical structure of the manganese
dioxide was determined by x-ray diffraction, electron diffraction, and electron microscopy. The
effectiveness of the product as a battery depolarizer was determined by making "A" size dry cells and
draining them at a prescribed rate.

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MANGANESE DIOXIDE

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ABSTRACT

The purpose of this investigation was to survey the field of chemical synthesis of manganese dioxide and to determine which syntheses might be adapted to commercial production of battery-active manganese dioxide.

Samples of manganese dioxide were prepared from chemical reagents by a large number of different syntheses. These samples were given a chemical analysis consisting of determination of total manganese, available oxygen, moisture content, and pH. The physical structure of the manganese dioxide was determined by x-ray diffraction, electron diffraction, and electron microscopy. The effectiveness of the product as a battery depolarizer was determined by making "A" size dry cells and draining them at a prescribed rate.

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INTRODUCTION

With the possibility of having the supply of battery-active manganese dioxide to the United States cut off in time of war, the necessity of developing methods of synthesizing a good manganese dioxide has become apparent. The United States does not have a natural source of battery manganese dioxide and has been importing a natural product from the Gold Coast of Africa.

As early as 1918 it was known that a battery manganese dioxide superior to natural Gold Coast ore could be prepared by electrolytic deposition of manganese dioxide on an anode. During the past several years the development of this method was accelerated under a program sponsored by the United States Army Signal Corps. At the present time commercial plants are being developed to prepare battery-active manganese dioxide by this method.

Although a superior product can be prepared by the electrolytic method, large quantities of electric power are required and the product is expensive. During any emergency which might develop, expansion of the industry would be limited to the amount of available power. Since large quantities of battery manganese dioxide are consumed, a more economical chemical process which will produce a depolarizer comparable to electrolytic methods is desired.

As early as 1913 patents have been obtained for chemical synthesis of manganese dioxide which was suitable for a battery depolarizer. Since that time practically all known methods of chemical preparation of manga-

nese dioxide have been reported as suitable for producing battery grade material. As there were no specifications for the requirements of battery depolarizer manganese dioxide until recently, many syntheses were reported which gave very poor depolarizers. The material from many of these syntheses was not as effective as natural Gold Coast ore.

The effectiveness of manganese dioxide as a depolarizer in dry cells can be determined only by actual testing of the cells. A group of preliminary tests will, however, give an indication of how the product will perform. These tests are: chemical analysis, x-ray diffraction, electron diffraction, and electron microscopy. Of these tests, the x-ray diffraction pattern has proved to be the most valuable means of determining crystalline phase.

The two crystalline phases of manganese dioxide are tetragonal (beta MnO_2) and orthorhombic (the mineral Ramsdellite). Five other phase types which are modifications of the basic phases are called alpha, gamma, delta, epsilon, and rho. In recent years tests conducted by the Squier Signal Laboratory of the United States Army Signal Corps at Fort Monmouth, New Jersey, have shown that gamma phase manganese dioxide has the structure best suited for battery depolarizer material. Rho manganese dioxide is a fair depolarizer about equivalent to Gold Coast ore. The other structures give very poor battery life.

The purpose of this investigation was to survey the field of chemical synthesis of manganese dioxide and to determine which syntheses might be adapted to commercial production of manganese dioxide comparable to the electrolytic product. Jack A. Davidson reported in a thesis the results of another group of manganese dioxide syntheses(4).

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EQUIPMENT, METHODS, AND SPECIFICATIONS

Equipment

Cell bobbin tamper

The inner bobbins for the test cells required a tamping machine and dies to form them to specifications. The tamping machine was hand operated and consisted of a tamper mounted on two vertical rods in such a way that it was free to move up and down. The stationary dies at the bottom were removable to facilitate cleaning. The lower stationary dies had bakelite inserts to keep the battery material from being contaminated by other metals and the tamper was made with a polystyrene tip for the same purpose. The use of dissimilar plastics prevented the tamper from binding when it was in the lower die. The bottom of the lower die was fitted with a plastic block which could be pushed up to force the completed bobbin out of the die. The upper end of this block was drilled to hold the carbon electrode centered in the die while the depolarizer mix was being tamped around it. The details of this tamper are shown in Figure 1.

Battery test rack

The testing of the dry cells consisted of discharging them through resistance coils. The high drain test used coils with 16 2/3 ohms resistance and the low drain test used coils with 166 2/3 ohms resistance. The test coils were hand wound of nichrome wire which had approximately 4.4 ohms resistance per foot and were calibrated with a Wheatstone bridge when they were installed in the test panel. The battery drain was recorded by taking voltage readings across the cells at intervals. The voltmeter

circuit used a Simpson Model 260 Volt-ohm-milliammeter and selector switches were used to switch from one cell to another. The test rack was capable of running four high drains and twelve low drains at the same time. A schematic drawing of part of the system is shown in Figure 2.

Chemical synthesis equipment

Standard chemical glassware was used as containers for most of the reactions and small electric stirrers were used to keep the materials mixed. A gas fired assay furnace was used for the high temperature heat treatments and the temperatures were measured with chromel-alumel thermocouples. Porcelain ball mills with quartz stones were used in all grinding operations. A thermostatically controlled electric oven was used to dry all samples and to give low temperature heat treatments.

Methods

Sample preparation

All of the samples were prepared from C.P. chemical reagents with the exception that a technical grade manganous sulfate was used in some cases. Small scale tests were usually run to see what conditions were necessary to make the reaction work and then a larger batch was made to give enough manganese dioxide for testing and analysis. All samples were dried at 110°C unless designated otherwise. The reactions used had either been suggested by the Army Signal Corps or were taken from literature (2,3,6). Since a variety of different methods of preparation were used, the preparation of each is given with the discussion of results.

Total manganese analysis

Approximately 0.1 gram of manganese dioxide sample was accurately

weighed and placed into a 600 ml beaker. Ten ml distilled water and five ml. concentrated hydrochloric acid were added and then boiled almost to dryness. The sample was taken from the heater and 25 ml concentrated sulfuric acid and 10 ml concentrated nitric acid were added. This mixture was heated until all of the brown fumes were expelled. The solution was cooled and diluted to 275 ml with distilled water. Approximately 3 grams sodium bismuthate were added and stirred until apparently all of the manganous ion had been converted to permanganate ion. The excess oxidant was filtered off with a fine sintered-glass filter and the filtrate was heated to $50^{\circ}C$. Fifty ml 0.2 N sodium oxalate solution was added and the excess titrated with 0.1 N potassium permanganate solution.

Available oxygen analysis

Approximately 0.2 gram of sample was weighed accurately and 50 ml 0.2 N ferrous ammonium sulfate solution containing 175 ml concentrated sulfuric acid per liter was added. The solution was diluted to about 200 ml with distilled water and digested on a steam bath until the sample was dissolved. A control sample was given the same digestion period and both samples were titrated with 0.2 N potassium dichromate solution using a potentiometric titration.

Determination of moisture

Between 1 and 3 grams of the original sample was dried for 16 hours at a temperature of $110^{\circ}C$. The loss of weight was taken as the water content of the sample.

Determination of pH

A sample between 0.8 and 1.0 gram was weighed into a 300 ml Erlen-

meyer flask and 100 times the sample weight of distilled water was added.
This solution was boiled for 20 minutes, the water level brought back to
the original and cooled to room temperature with an ascarite tube over it
to prevent contamination from carbon dioxide in the air. The pH of the
supernatant liquid was determined with a Beckman pH meter.

Determination of bulk density

The bulk densities of the samples were determined with a standard
Scott paint volumeter. The sample was poured through the volumeter until
the cubic inch cup was full, the excess was scraped off with a spatula,
and the weight of the manganese dioxide in the cup was the density in grams
per cubic inch.

Determination of battery capacity

Five standard "A" size dry cells were constructed according to exist-
ing dry cell assembly techniques from each sample. The cells were stored
from four to five days at room temperature (65-75°F) before being discharged.
Two cells were discharged continuously through 16 2/3 ohms for the high drain
test and two were discharged continuously through 166 2/3 ohms for the low
drain test. The fifth cell was set aside for three months before it was
given the low drain test.

Specifications

The following specifications for synthetic battery-active manganese
dioxide were taken from Army Signal Corps Tentative Specification (1):

Chemical composition

Available oxygen as % MnO_2	85% min.
Total manganese as % Mn	58% min.

Absorbed moisture as % H_2O	3% max.
Iron as % Fe	0.2% max.
Silicon as % SiO_2	0.5% max.
Other metallic impurities	0.1% max.
pH	4.0-8.0

Crystalline phase

X-ray diffraction patterns should show a predominance of the imperfectly crystallized phase known as gamma manganese dioxide. A chart showing the x-ray diffraction pattern of the various phases is given in Figure 3.

Battery capacity

The standard "A" size dry cell, when fabricated according to specifications, shall run a minimum of 5.50 hours on high drain test and 130 hours on low drain test. Cutoff voltages were respectively 1.00 and 1.13.

Density

The bulk density of the product as measured by the Scott volumeter shall be a minimum of 20 gm/in^3. This density should give a cell bobbin weight which is between 9.5 and 10.5 grams.

DISCUSSION OF RESULTS

Nitric acid oxidation of hausmannite (Mn_3O_4)

The hausmannite used in this reaction was obtained either by heating inactive reagent manganese dioxide or technical manganous sulfate in a furnace at 1000-1100°C for 4-5 hours according to the reactions:

$$3MnO_2 \xrightarrow{\Delta} Mn_3O_4 + O_2$$

$$3MnSO_4 \xrightarrow{\Delta} Mn_3O_4 + O_2 + 3SO_2$$
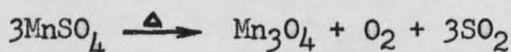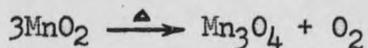
The hausmannite formed from these reactions was reoxidized to manganese dioxide by treatment with nitric acid according to the reaction:

$$Mn_3O_4 + 4HNO_3 \longrightarrow 2Mn(NO_3)_2 + MnO_2 + 2H_2O$$
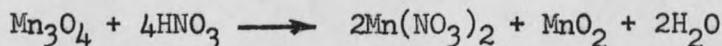
The preparation of each sample is given in Table I.

Since two-thirds of the manganese was dissolved in the nitric acid, the degree of oxidation of the hausmannite was proportional to the loss of weight of the solid material. The data supported this fact, because only samples which had high losses met specifications for oxygen content. To obtain a high oxidation it was necessary to grind the hausmannite to -150 mesh before treatment with nitric acid, as shown by the chemical analysis (Table II) of samples O-H-7, O-H-8, and O-H-9.

Although particle size has some effect on the required temperature, it was apparent that the mixture had to be heated above 75°C before any appreciable reaction took place. When the reaction started, it was exothermic and the temperature was difficult to control until most of the oxidation had taken place. The reaction time to produce the best samples was $1\frac{1}{2}$ hours, but since no attempt was made to reduce the time with finely ground hausmannite, there was a possibility that a shorter time could be

used. The oxidation reaction above was given in Curtman (3) using any acid, so attempts were made to use a portion of sulfuric acid. Although up to 10% sulfuric acid by volume did not cause an appreciable change in the product, 50% sulfuric acid lowered the oxidation and cut battery life. Hydochloric acid was not used for this reaction because it dissolves manganese dioxide.

The physical properties of this product were good. It gave a high density product unless the hausmannite was ground extremely fine, and tamped into a cell bobbin which met weight specifications in most cases (Table III). The proper pH of the finished samples were easily obtained by washing the product in water.

Micro-optical analysis of the materials have shown that the predominant phase in the poorly oxidized samples was hausmannite with minor phases of rho-gamma. Although four of the samples were reported with a major beta phase, the original manganese dioxide which was beta was only given a moderate heat treatment for two of these samples. The other two samples with beta phase probably were partly formed from decomposition of the manganous nitrate which formed as a byproduct.

The battery drain tests on this material did not meet specifications but the 5.1 hours on high drain was the best obtained from any product made by chemical methods. The low drain tests reached a maximum of 110 hours. An attempt to improve the battery life by grinding the products made from a coarse hausmannite failed to show any appreciable difference. It was noted that materials which were below specifications for available oxygen gave good battery tests if the proper crystalline phase was present (O-H-5).

Only three samples were prepared from hausmannite made from manganous sulfate. Since none of the samples had been prepared at temperatures above 85°C, no comparison can be made with the products described above. The sample prepared at 85°C gave a fairly good battery test of 107 hours on low drain and 2.2 hours on high drain, and was the best of the three samples. All of the samples gave gamma-rho x-ray diffraction patterns.

Although the losses of manganese are high in each batch process, a nitric acid cycle could be set up whereby the nitric acid and the manganese could be recovered and recycled.

Chlorine oxidation of manganous carbonate

The chlorine oxidation of manganous carbonate took place in an aqueous suspension according to the equation

$$MnCO_3 + Cl_2 + H_2O \longrightarrow MnO_2 + 2HCl + CO_2$$

Since the solubility of gaseous chlorine in water was inversely proportional to the temperature, the reaction proceeds much faster at low temperatures.

Only one of the samples made by this method was good on battery tests (C-CL-3) but this was enough to make the reaction look promising. This sample had a density of 17.3 gm/in^3 and was completely reacted to manganese dioxide, while other samples made in the same way except for an hour longer reaction time were of very low density. The only explanation for this difference is that reaction time seems to be very critical.

The first sample prepared by this method was washed with nitric acid to remove any manganous carbonate and to complete the oxidation. This gave beta manganese dioxide, while the other samples were in the gamma-rho

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structure range except where heat treatments decomposed residual manganous carbonate. The acid treatment appeared to have converted the gamma-rho to the beta phase.

A large sample was split into four parts and three of these were given heat treatments at 150, 170, and 200°C to investigate the possibility of converting rho or rho-gamma manganese dioxide to the gamma phase. Since the x-ray diffraction patterns were very similar between gamma and rho (Figure 3), there seemed a possibility of converting from one to the other. Although the battery tests were very poor, there was some improvement in material heated at 170°C and this agreed with heat treatment of other rho-gamma products as reported by Davidson (4).

As a result of these heat treatments some residual manganese carbonate was converted to beta manganese dioxide almost in proportion to the temperature. This result agreed with the findings of Davidson(4) for a synthesis by this method.

Decomposition of manganous nitrate

When heated at temperatures above 150°C, solutions of manganous nitrate decomposed according to the equation:

$$Mn(NO_3)_2 \xrightarrow{\Delta} MnO_2 + 2NO_2.$$

The product from this reaction had a high density and in most cases was a high percentage manganese dioxide.

The crystalline phase of material produced by this reaction was predominantly beta with traces of rho and the battery life was only about half of the specifications. Although Nossen (5) reported that gamma manganese dioxide was produced by this type of reaction, none has been syn-