Battery active manganese dioxide by chemical synthesis
by William G Moore

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering at Montana State College
Montana State University

Abstract:
The reagents chlorine, sodium hydroxide, and manganese sulfate have been reacted by several techniques to yield manganese dioxide. The manganese dioxide was tested according to the U. S. Army Signal Corps specifications SCL-3H7-D for utility as a high grade depolarizer for Leclanche dry cells. The promising reactions were investigated extensively and treatment effects evaluated.

The synthesis methods investigated were: 1. Chlorine oxidation of manganese hydroxide 2. Chlorine oxidation of manganese sulfate 3. Basic hypochlorite oxidation of manganese sulfate 4. Miscellaneous methods which incorporate combinations of the first three methods Data on chemical and physical properties of the MhO2 together with X-ray diffraction analyses and battery tests are reported. Analysis of synthesis methods and operational difficulties are discussed.

The chlorine oxidation of manganese hydroxide was scaled up to 200 gallon semi-continuous operation with commercial reagents. The better runs yielded manganese dioxide which passed the chemical and drain test requirements of the Signal Corps Specification 31177-D for synthetic MnOg for military grade dry batteries. Analysis by X-ray diffraction shows the MhOg to be of the gamma-rho to rho crystalline structure.

Blends of Gold Coast ore and manganese dioxide prepared in the scaled up reactions were tested for indications of the commercial utility of the chemical depolarizer. A mutual upgrading effect is shown by the Gold Coast-chemical..ore blend in contrast to the linear variation of battery life with composition exhibited by electrolytic Mn02-Gold Coast ore blends. Specification battery tests are obtained with 55%-60% chemical ore, whereas 85-90% electrolytic ore is required! to upgrade Gold Coast ore to the same capacity.

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ABSTRACT

The reagents chlorine, sodium hydroxide, and manganese sulfate have been reacted by several techniques to yield manganese dioxide. The manganese dioxide was tested according to the U. S. Army Signal Corps specifications SCL-3117-D for utility as a high grade depolarizer for Leclanche dry cells. The promising reactions were investigated extensively and treatment effects evaluated.

The synthesis methods investigated were:

1. Chlorine oxidation of manganese hydroxide
2. Chlorine oxidation of manganese sulfate
3. Basic hypochlorite oxidation of manganese sulfate
4. Miscellaneous methods which incorporate combinations of the first three methods

Data on chemical and physical properties of the MnO_2 together with X-ray diffraction analyses and battery tests are reported. Analysis of synthesis methods and operational difficulties are discussed.

The chlorine oxidation of manganese hydroxide was scaled up to 200 gallon semi-continuous operation with commercial reagents. The better runs yielded manganese dioxide which passed the chemical and drain test requirements of the Signal Corps Specification 3117-D for synthetic MnO_2 for military grade dry batteries. Analysis by X-ray diffraction shows the MnO_2 to be of the gamma-rho to rho crystalline structure.

Blends of Gold Coast ore and manganese dioxide prepared in the scaled up reactions were tested for indications of the commercial utility of the chemical depolarizer. A mutual upgrading effect is shown by the Gold Coast-chemical ore blend in contrast to the linear variation of battery life with composition exhibited by electrolytic MnO_2-Gold Coast ore blends. Specification battery tests are obtained with 55%-60% chemical ore, whereas 85-90% electrolytic ore is required to upgrade Gold Coast ore to the same capacity.

INTRODUCTION

The need for portable power sources has been satisfied by a variety of cell systems. Many of these cells utilize an oxidation-reduction reaction which features solution of a metal to yield metal ions at one electrode and evolution of hydrogen at the other electrode.

Researchers soon discovered that the evolution of hydrogen was undesirable, since it caused the cell potential to fall rapidly even when the current drain on the cell was light. This phenomenon, which caused a voltage decrease when the cell was under current drain, was termed polarization. Elimination of polarization, or depolarization, became the object of intensive study. Depolarization by reacting the hydrogen with an ozidizing agent to form inert reaction products was the approach which led to eventual success. The oxidizing agent which proved most efficient from the point of view of stability, availability, and effectiveness was the oxide of tetravalent manganese, manganese dioxide. Best known of manganese dioxide depolarized dry cells is the Leclanche dry cell, which utilizes the carbon-manganese dioxide: zinc metal couple.

Large naturally occuring deposits of high quality battery active manganese dioxide in Western Africa were instrumental in the success of the Leclanche cell. Note that the African natural manganese dioxide is described as battery active, implying that high quality MnO_2 exists which is not battery active, i.e., does not function well as a depolarizer despite its high assay of MnO_2.

Investigations by battery manufacturers and independent researchers led to improvements in dry cell manufacturing techniques, formulations, and storageability, but no significant improvement in the depolarizer was made as long as the Gold Coast ore was available to the world at a reasonable price. Other MnO_2 ores were evaluated as were a variety of synthetically prepared dioxides, but most were found to be inferior to Gold Coast ore in performance. Some investigators began to discover that the common denominator of battery activity of manganese dioxide was a rather nebulous sort of thing. When the analytical tools of X-ray diffraction and electron microscopy were brought to bear, the problem of differentiating battery active MnO_2 from the inactive dioxide began to be resolved. In general, the well defined, highly crystalline species which gave sharp diffraction patterns were poor depolarizers, while the active species tended toward an amorphous or meso crystalline structure and are characterized by diffuse diffraction patterns.

As an introduction to the use of electron micrographs and X-ray diffraction in evaluating battery active MnO_2, the reader is referred to Figures 1 through 8. Figure 1 was prepared by the micro-optical section of the Signal Engineering Laboratories as a guide in judging the merits of synthetic MnO_2. The gradations in crystal habit correlate rather well with battery activity for MnO_2 having similar chemical and physical properties such as $\%MnO_2$, free moisture, apparent density, and crystal phase.

The electron micrographs must be used in conjunction with the other analytical procedures to avoid unwarranted conclusions as the following instances will illustrate:

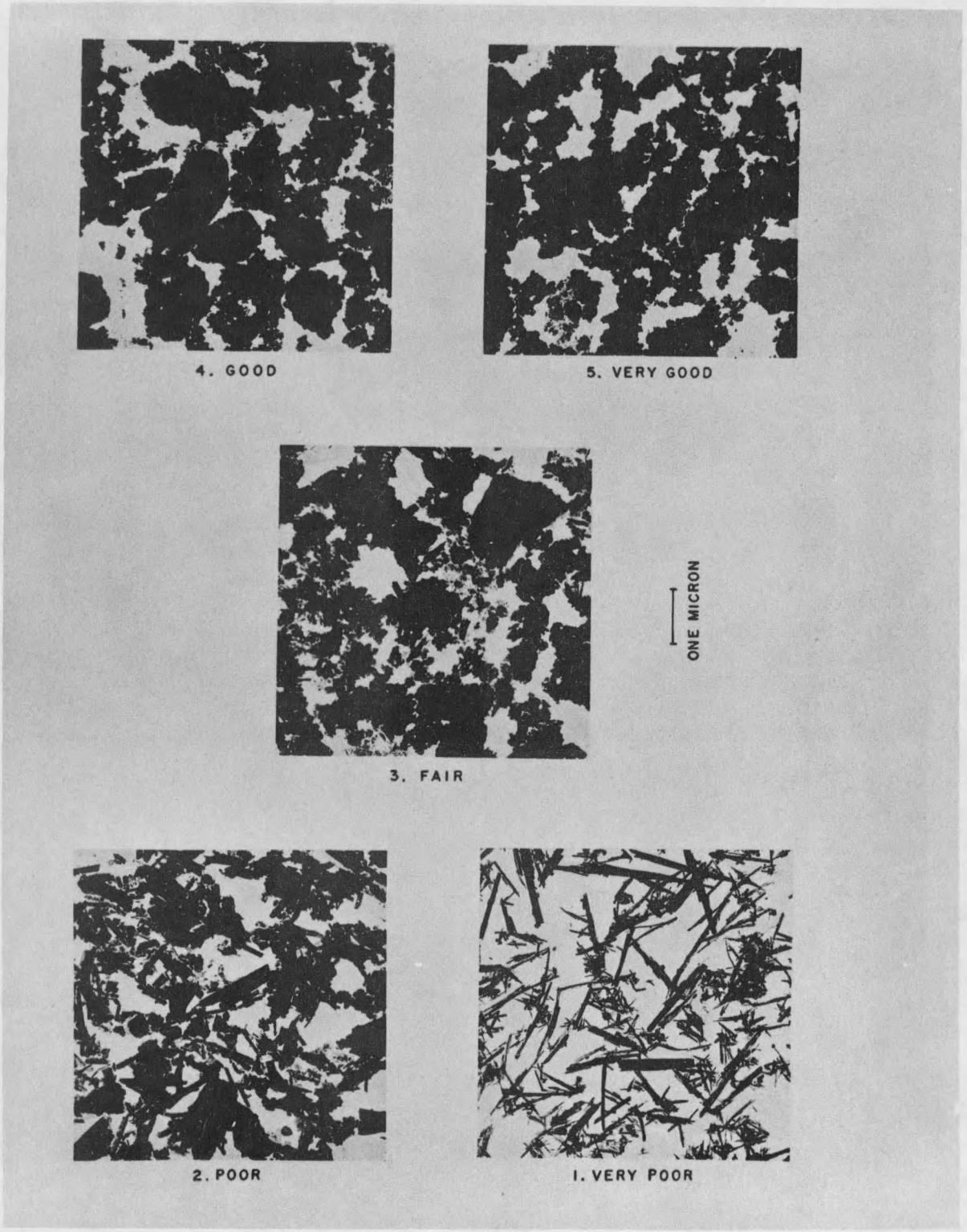

Figure 1 Reference Electron Micrographs

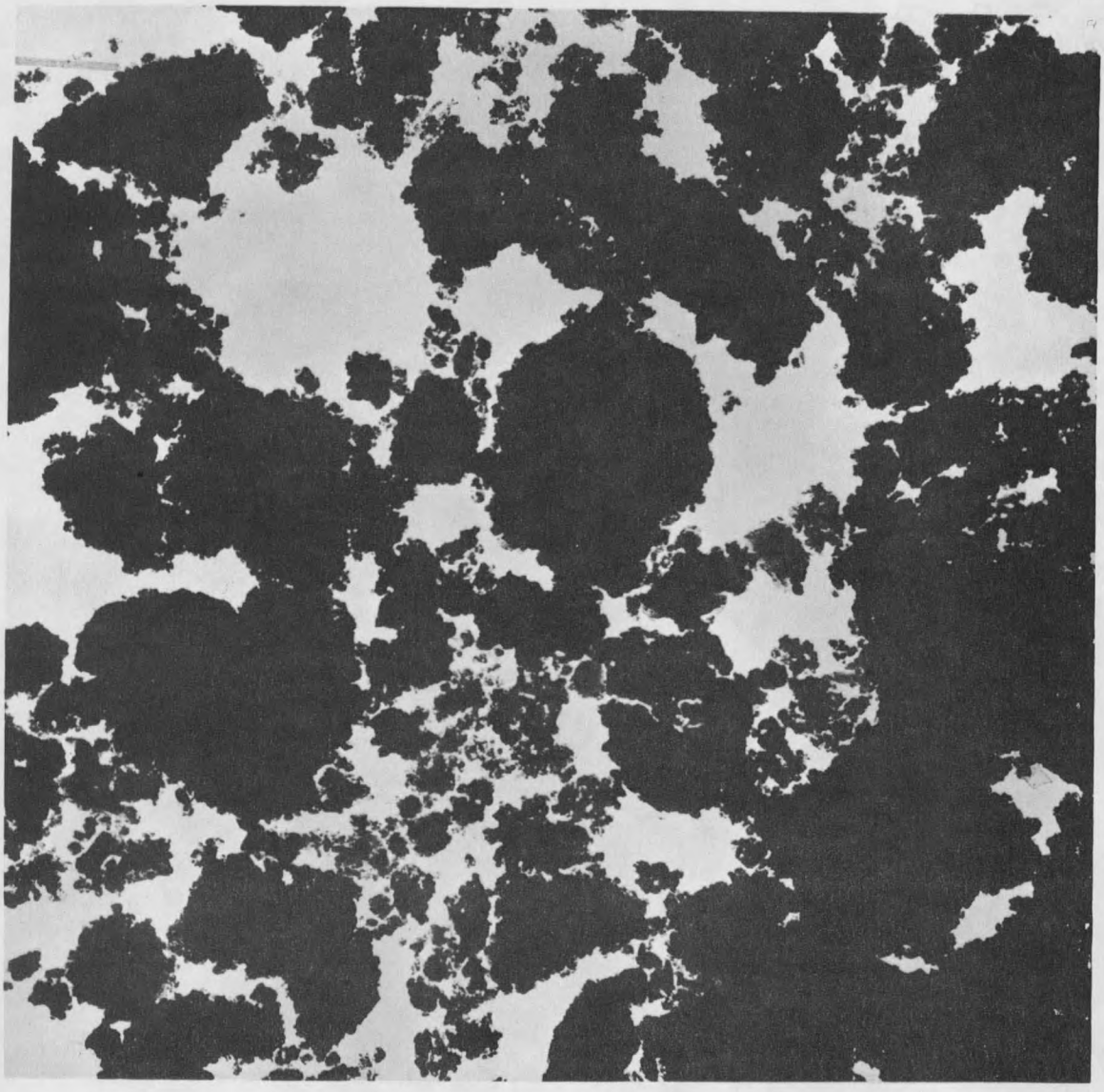

Figure 2 Electron Micrograph MnO_2 32,000X

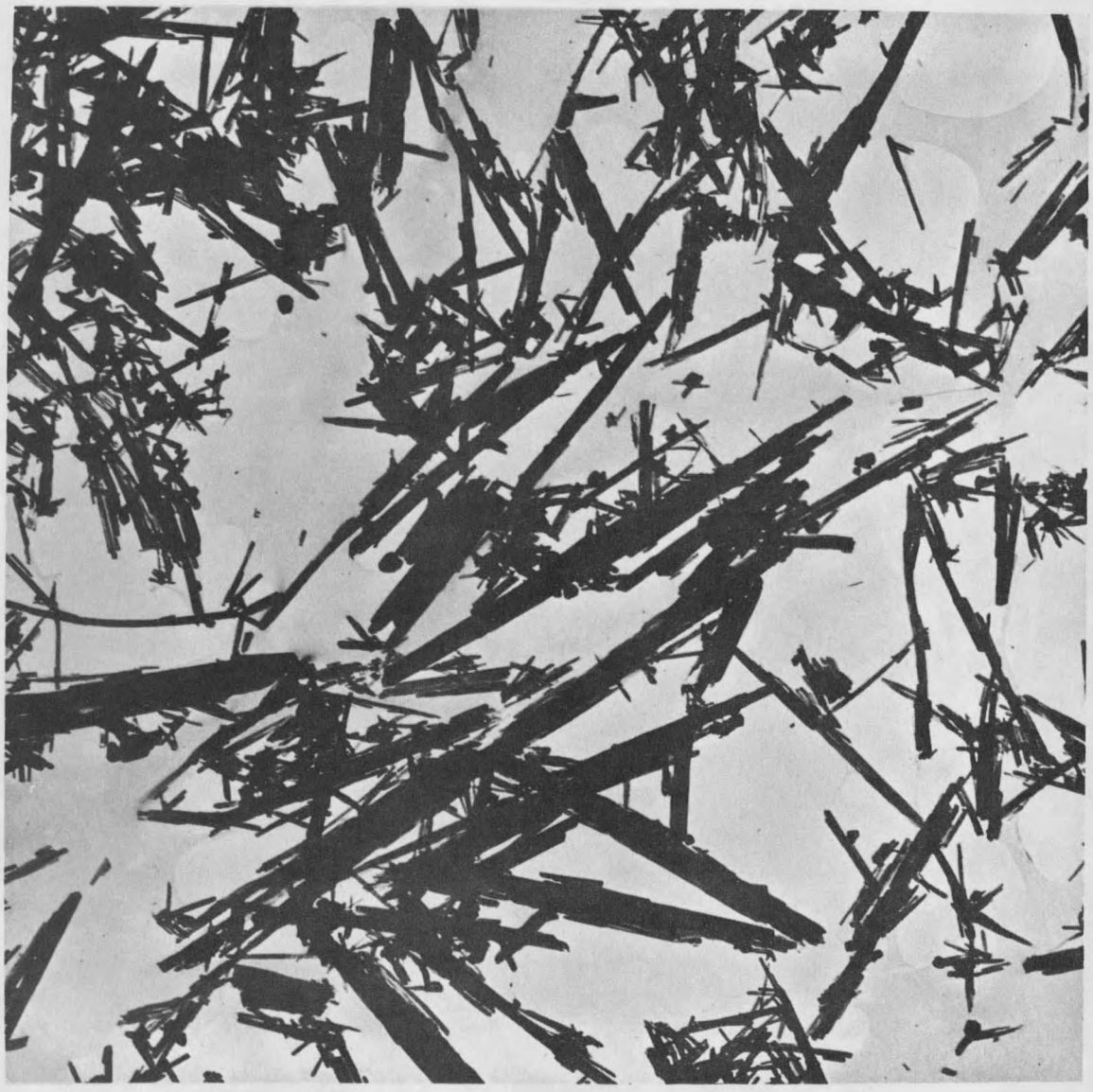

Figure 3 Electron Micrograph of MnO_2 - 32,000X