

AD-A185 919

AN INVESTIGATION OF THE RECHARGABILITY OF CERTAIN  
MODIFIED FORMS OF HNO<sub>2</sub>(U) EMENTECK INC COLLEGE STATION  
TX A J APPLEBY 30 SEP 87 N00014-87-C-0662

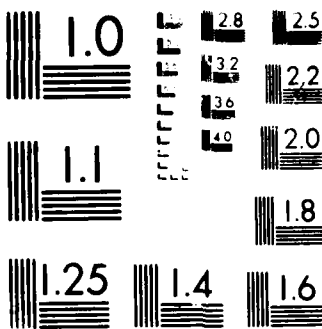
1/1

UNCLASSIFIED

F/G 10/3

ML





RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

DTIC FILE COPY

**EMENTECK, INC.**

(12)

RT. 5 BOX 946B  
COLLEGE STATION, TX. 77840  
(409) 845-5335

**AD-A185 919**

September 30, 1987

**DTIC**  
**ELECTE**  
NOV 09 1987  
**S** **D**  
C&H

Attn: Dr. Robert Nowak, Code 1113ES  
Office of Naval Research  
800 North Quincy Street  
Arlington, VA 22217-5000

Subject: "An Investigation of the Rechargability of Certain Modified Forms of MnO<sub>2</sub>"  
Contract No. N00014-87-C-0662  
First Quarterly Report, September 30, 1987

Dear Dr. Nowak:

Please find enclosed the first quarterly letter report under the subject contract.

Introduction

The contract commenced on July 1, 1987, and emphasis has so far been on the procurement of the necessary equipment and materials to fulfill the terms of the Statement of Work. The latter presents a general proposal on the desirable experimental work that should be accomplished to determine the feasibility of, and the scientific reasons for, a two-electron charge-discharge capability of modified manganese dioxide of birnessite type.

This material has the approximate formula  $M_xMnO_y$ , associated with some lattice water, in which M is bismuth or lead, x is in the range 0.06 to 0.14, and y is correspondingly 2.08 to 2.21. Such stabilized birnessite compounds were first prepared at the Ford Motor Company, as described in U. S. Patent Application Serial No. 548,070 (Nov. 2, 1983), later abandoned, and continuation-in-part application No. 668,544 (Nov. 5, 1984) issued as Pat. No. 4,520,005 (May 28, 1985). The rechargeability of such materials was described in Applications Nos. 521,473; 521,474 (Aug. 8, 1983), and a method of making a rechargeable zinc-modified manganese dioxide cell was the subject of Application No. 537,206 (September 29, 1983; issued as Patent No. 4,451,543; May 29, 1984). Work at Ford showed that the birnessite-type material could be cycled at high rates in alkaline medium in thin electrodes against suitable counter-electrodes, for example

**DISTRIBUTION STATEMENT A**

Approved for public release;  
Distribution Unlimited

**87 107 054**

allowing 12 Amp/g complete discharges (essentially two electrons), or a rate of about 6C. Rechargeability was shown to be good, with good overcharge-overdischarge protection and the capability of complete discharge under the same conditions as primary alkaline cells (up to approximately two electrons) with no lattice degradation. 2500 voltammetric cycles were demonstrated in laboratory equipment to 80% of theoretical two-electron capacity (TTC) under these conditions, followed by voluntary disconnection. In contrast to this performance, all previous attempts to discharge any  $MnO_2$  variety (and still maintain a degree of rechargeability, e.g., up to some 60 cycles) required a depth of discharge not exceeding 15% of TTC. This has made the rechargeable Zn- $MnO_2$ -alkaline system very unattractive.

### Objective of Present Contract

The objective of the present contract, as set out in the generalized statement of work representing a long-term project, is to perform work on the development of a high-rate rechargeable zinc-manganese dioxide system based on Ford's technology (for example, U. S. Patent No. 4,451,543) and to examine the possibility of a rechargeable lithium-organic electrolyte intercalation-type system using birnessite  $MnO_2$  compounds. In addition, some studies on the structures of compounds will be carried out, as may be possible according to the technical means available, on the scientific reasons for the rechargeability of birnessite. Examples of scientific techniques that may throw light on this were quoted in the statement of work as Fourier-Transform Infra-Red Spectroscopy (FTIR), X-ray diffraction and EXAFS. Since the compound is an amorphous powder with a surface BET area of about  $50 \text{ m}^2/\text{g}$ , we have determined that FTIR and X-ray diffraction are unlikely to be appropriate for this purpose, and that EXAFS represents the method that is most likely to yield useful data on cells in different states of charge. The method also has the advantage of being usable in-situ. Unfortunately, beam-time on either the National Photon Source at Brookhaven or the Stanford Synchrotron is unlikely to be available before the end of 1988. The best plan will be to use the National Source, which is available free or at low-cost for academic researchers, whereas commercial users conducting proprietary work are required to pay a charge which may exceed \$50,000. In consequence, this EXAFS work will be conducted under the auspices of Texas A&M University when beam-time is available, and a separate addendum to the final report of this contract will be made available to the Procurement Office.

Work to be performed under Contract No. N00014-87-C-0662 will therefore concentrate on practical approaches to high-rate rechargeable zinc-modified  $MnO_2$  and lithium-modified  $MnO_2$  batteries. At the Ford Motor Company, most long-term cycling involved voltammetric

discharge/charge, and attempts to construct complete laboratory battery hardware were limited. However, the fact that zincate ion (the discharge product of the zinc electrode) was detrimental to charge-discharge behavior of birnessite  $\text{MnO}_2$  in 9M KOH was noted in U. S. Patent No. 4,451,543. Best results were obtained using selected separators, preferably Daramic (porous polypropylene), with the addition of equal volume mixtures of methanol and the 9M KOH electrolyte. The addition of methanol depresses zincate solubility, which seriously interferes with birnessite charging. Even so, the result is a serious reduction in capacity to only 25% of the available 2-electron value after about 50 cycles. This clearly requires extensive work if rechargeable Zn-modified  $\text{MnO}_2$  cells are to be practical. In contrast, while other negative couples may be possible (for example, cadmium or iron), which have very insoluble discharge products compared with zinc. However, their disadvantages of heavier weight, and lower, non-standard voltage of 0.4V below that of the Zn- $\text{MnO}_2$  couple, and in the case of iron poor coulombic characteristics on charge, make them unattractive.

The organic electrolyte system using a lithium negative and propylene carbonate electrolyte has been examined at Ford and showed rechargeability. However, it is well known that propylene carbonate is not an ideal solvent for rechargeable lithium systems, and ethers, esters or their mixtures (such as methyl tetrahydrofuran and suitable derivatives, methyl acetate and other esters) along with  $\text{LiAsF}_6$  or  $\text{LiPF}_6$  appear to be most appropriate. These will be explored in button cells, prepared under dry-box conditions, with careful attention paid to the preliminary dehydration of birnessite  $\text{MnO}_2$ .

#### Work Conducted, July 1, 1987 - September 30, 1987

- 1) Major progress has been made regarding reproducing the method of fabrication of the  $\text{M}_x\text{MnO}_y$  class of compounds using the methods disclosed in U. S. Patent No. 4,520,005.
- 2) Cells for preliminary cycling and dies for pressing electrodes have been designed and have been fabricated. Testing of birnessite positives in 9M KOH has been initiated to reproduce the charge-discharge properties in the absence of zincate ions obtained at the Ford Motor Company. Such cycling uses nickel counterelectrodes.
- 3) A search for other additives to suppress zincate concentration has been initiated. These will include a proprietary mixture of compounds producing a reticulated polymer that traps zincate in colloidal form, preventing its transfer into the birnessite. In addition, variation of KOH or other

alkali concentration will be made to change zincate solubility characteristics.

- 4) During the next reporting period, cycling characteristics under high-rate conditions will be determined and a start will be made on the examination of lithium organic cells.

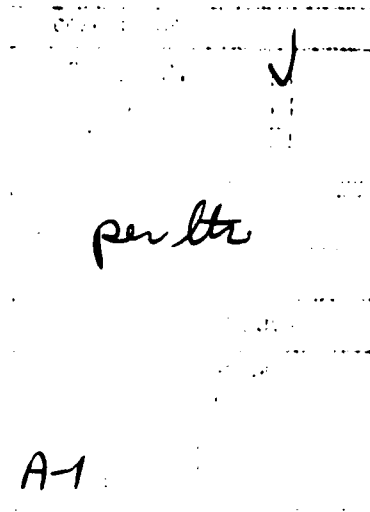
Distribution

Administrative Contracting Officer, S4404A 1 copy

Sincerely,



A. J. Appleby  
President, Director of Research



per ltr  
A-1

END

DATE

FILMED

JAN

1988