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CADMIUM ELECTRODE INVESTIGATION

EAGLE-PICHER INDUSTRIES, INC.
ELECTRONICS DIVISION
COUPLES DEPARTMENT
JOPLIN, MO. 64801

MARCH 1980

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Final Report for period July 1979 — December 1979

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Robert L Kerr

R.L. KERR
Project Engineer

Robert R Barthelemy

ROBERT R. BARTHELEMY
Chief, Energy Conversion Branch

FOR THE COMMANDER

JAMES D. REAMS
Chief, Aerospace Power Division

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Methods for improving the loading and utilization of active material in electrochemically impregnated cadmium electrodes were studied using sweep voltametry and galvanostatic pulse impregnation. Loading levels and utilization were found to decrease with cycling when the potentiostatic pulse method was used and impregnation times beyond one hour resulted in unacceptable surface loading. The use of galvanostatic pulse impregnation appeared to offer greater promise; however, solution composition, temperature and the pulse regime remain to be optimized. Several areas are recommended for further study including understanding

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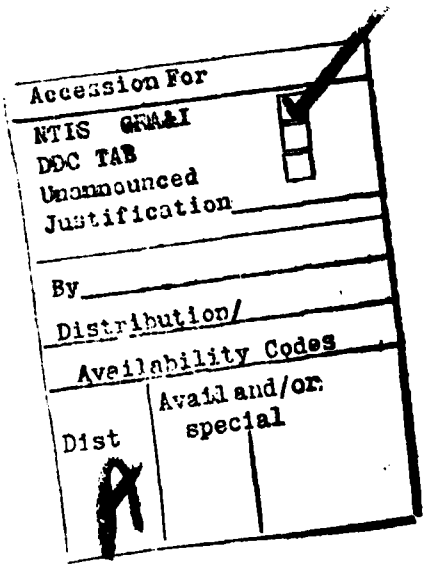
of the cathodic processes, the economics of the counter electrode, solution pH control, definition of the process parameters and the effect of plaque pore morphology on loading efficiency.

PREFACE

This report documents the effort conducted by Eagle-Picher Industries, Inc., in compliance with contract F33615-79-C-2056. Submission of this report is to the Air Force Wright Aeronautical Laboratories, AFSC, Wright-Patterson AFB, Ohio in accordance with contract requirements. The contract was initiated in July 1979 and completed in December 1979. The objective of the contract was to investigate methods for loading and utilization of active material in electrochemically impregnated cadmium electrodes.

We wish to acknowledge and greatly appreciate the guidance and support of R. L. Kerr of the Aero Propulsion Laboratory, under whose direction the contract was performed.

At Eagle-Picher Industries, Inc., the contract was under the management of Dr. E. Buck.



The minielectrode used for these studies was fabricated from a standard Eagle-Picher dry sinter nickel plaque. This plaque had the following properties:

Thickness	0.026 in
Porosity	79.0 %
Pore Volume	0.423 cc/g
Average Pore Diameter	12.5μ
Specific Surface Area	0.220 m^2/g

The plaque was coined (see coining die figure) to give plates 0.5" x 0.5" with an uncoined area of 1.35 cm^2. Nickel tabs were fusion welded to the plates and were enclosed with polypropylene shrink tubing from the plate to within approximately ½" of the free end. The plates were finished by edging with latex applied as a water emulsion. The plates, now minielectrodes, were degreased in trichloroethane and in isopropanol and finally dried in a vacuum oven before use.

The impregnation solution was a 2M cadmium nitrate solution prepared from reagent grade $Cd(NO_3)_2$ and deionized water. The pH of this solution varied from lot to lot and was about 2.3. Solution pH was not adjusted.

Most electrochemical measurements were made in a 50 ml Metrohm polarographic style cell using a platinum gauze counter electrode and a saturated calomel reference electrode. The SCE was isolated from the test electrode compartment with a salt bridge having a porous Vycor frit at each end. The test solution was deaerated with and maintained under a He atmosphere. Test solution temperature was controlled using a Nesslab RTE-8 constant temperature circulator.

All voltammetric and galvanostatic experiments were performed with a Stonehart Associates BC-1200 potentiostat, a PAR waveform generator, a PAR digital coulometer, a Hewlett-Packard X-Y recorder, associated meters and

scope. The potentiostat was used in a positive feedback mode for IR compensation in the sweep voltammetry experiments. For the galvanostatic pulse experiments, the IR-bridge compensation network was employed.

Plate capacities were measured by charging and discharging the plate against a nickel sheet counter electrode. Charging was done at a C/4 rate; whereas discharge was at a C/2 rate to 1 V versus a half charged nickel oxide electrode. All cycling was done in 30% KOH solution.

The current-potential characteristics of the porous minielectrodes in 2M $Cd(NO_3)_2$ are strongly temperature dependent. Linear sweep voltamograms were done at 25°C and 75°C. Those done at 25°C were of the same shape as obtained by Maloy (Ref 1) provided that the sweep rate was no higher than 2mv/sec. Similarly obtained voltamograms obtained at 75°C were quite different. The current potential characteristic was almost featureless going smoothly into background at about -700mv versus SCE.

Potentiostatic pulse regimes were used for loading experiments at both 25°C and 75°C. For the 25°C experiments the plate was initially plated with Cd at -650mv vs. SCE to the extent of about 1 coulomb of charge. Plates (both 25°C and 75°C) were then pulsed on a 10 second cycle; 9 sec. at -1000mv versus SCE then 1 sec. at -100mv versus SCE. Pulsing was continued until a net charge of 205 coulombs had been cathodically applied.

The electrodes pulsed at 25°C exhibited a dense, electrochemically inactive deposit that was essentially surface loading. The Cd deposits were not accessible at viable charge/discharge rates in 30% KOH.

Plates loaded by potentiostatic pulsing at 75°C did load effectively. There was some surface loading as evidenced by a plate thickening of 2 to 3 mils. The results were as follows:

	1st Discharge	2nd discharge
Net loading on impregnation, coul.	205	
discharge capacity, coul.	151	126
discharge capacity, mahrs	42	35
discharge capacity, mahrs/cm^2	31	26
discharge capacity, mahrs/in^2	200	124
discharge capacity, mahrs/cc of pore vol.	471	393
discharge capacity, AH/cu in. of pore vol.	7.7	6.4
loading efficiency, %	74	61

The two immediately obvious facts concerning this impregnation are that the loading level is relatively low and that the utilization decreases with cycling. The total impregnation time was arbitrarily limited to one hour. Longer loading times in a potentiostatic regime resulted in unacceptable surface loading.

Galvanostatic pulse impregnation following the pulse regime of Fritts (Ref.2), was partially evaluated. Our standard 0.21 in^2 minielectrode was impregnated in 2M $Cd(NO_3)$ of pH about 3.0 and pulsed at 42 ma (0.2A/in^2) in a one minute cycle comprised of 50 sec. cathodic current and 10 sec. of anodic current. The electrode was, as for the potentiostatic case, impregnated to a net of 205 coulombs. The potential excursions of the minielectrode vs. a SCE electrode were recorded during the two hour impregnation. Initially, the cathodic potential excursions were to about -600mv but increased gradually to over -1.2V vs. SCE as the impregnation progressed. The shape of the potential response is interesting in that the cathodic polarization decreased from the beginning of a cathodic pulse to the end of the pulse. Some difficulty was encountered with the salt bridge in this experiment - bubbles - but that did not affect the potential response shape.

Plates were effectively loaded at 75°C using the above galvanostatic pulse regime. Surface loading was minimal, i.e. 1 to 2 mils thickening. Results are as follows:

	1st Discharge	2nd Discharge
Net loading or impregnation, coul.	205	
discharge capacity, coul.	153	131
discharge capacity, mahrs	42.5	36.4
discharge capacity, mahrs/cm^2	31.5	27.0
discharge capacity, mahrs/in^2	203	174
discharge capacity, mahrs/cc of pore vol.	476	408
discharge capacity, AH/cu in. of pore vol.	7.8	6.7
loading efficiency, %	74.6	63.9

The galvanostatic pulse impregnation yields slightly higher utilizations than does the potentiostatic loading on both the 1st and 2nd discharge cycles.

Two other galvanostatic impregnation regimes were cursorily evaluated. The case in which cathodic current was continually applied produced electrodes with unacceptable surface loading. A pulse regime in which the current was only interrupted as opposed to being reversed produced electrodes not sensibly different from those from the above reversal techniques. It would thus appear that the only benefits accruing from a current reversal technique are obtained at the counter electrode. No evidence was obtained in this brief study to either substantiate or deny the proposed deposition mechanism of Maloy, et al. It must be understood that potential cannot be completely controlled at a porous electrode except under equilibrium conditions due to the IR drop in the electrode itself. The general shape of the current potential characteristic of the porous electrode is quite similar to that of the plane electrode only in the case of very slow scan rates and even then it is distorted to an extent that is not readily correctable.

The galvanostatic pulse regime appears to be a suitable impregnation procedure, however, specific parameters must still be specified. Neither the solution composition, nor the temperature, nor the pulse regime have been optimized. If such an impregnation procedure is indeed to be advocated, each of these parameters and their interaction need to be studied in a full fledged effort.

Unfortunately, no part of this effort was allotted to the basic question of a counter electrode. It has been tacitly assumed in the statement of work that a Cd counter electrode would be used in any commercialization of this technique. This premise must be carefully evaluated. The apparent simplicity of solution maintenance with a Cd counter electrode must be weighed against the difficulty of a current reversal scheme involving thousands of amps. The most usual argument of solution depletion during impregnation simply will not hold since less than one gallon of 2M solution is sufficient to fully load a typical 100 in^2 plate with only a 10% change in Cd ion concentration. Control of solution pH is difficult regardless of the counter electrode used.

Areas requiring further study are:

1. A clearer understanding of the cathodic processes must be established.
2. The economics of the counter electrode should be investigated to answer the question of whether a cadmium electrode vs. an inert electrode should be used.
3. It should be determined whether a buffer system such as the NO_2/NO_3 system of the Bell method for nickel electrodes should be employed to control pH.
4. The process parameters such as solution composition, temperature and current regime should be defined in order to optimize loading.
5. The effect of plaque pore morphology on loading efficiency should be determined.

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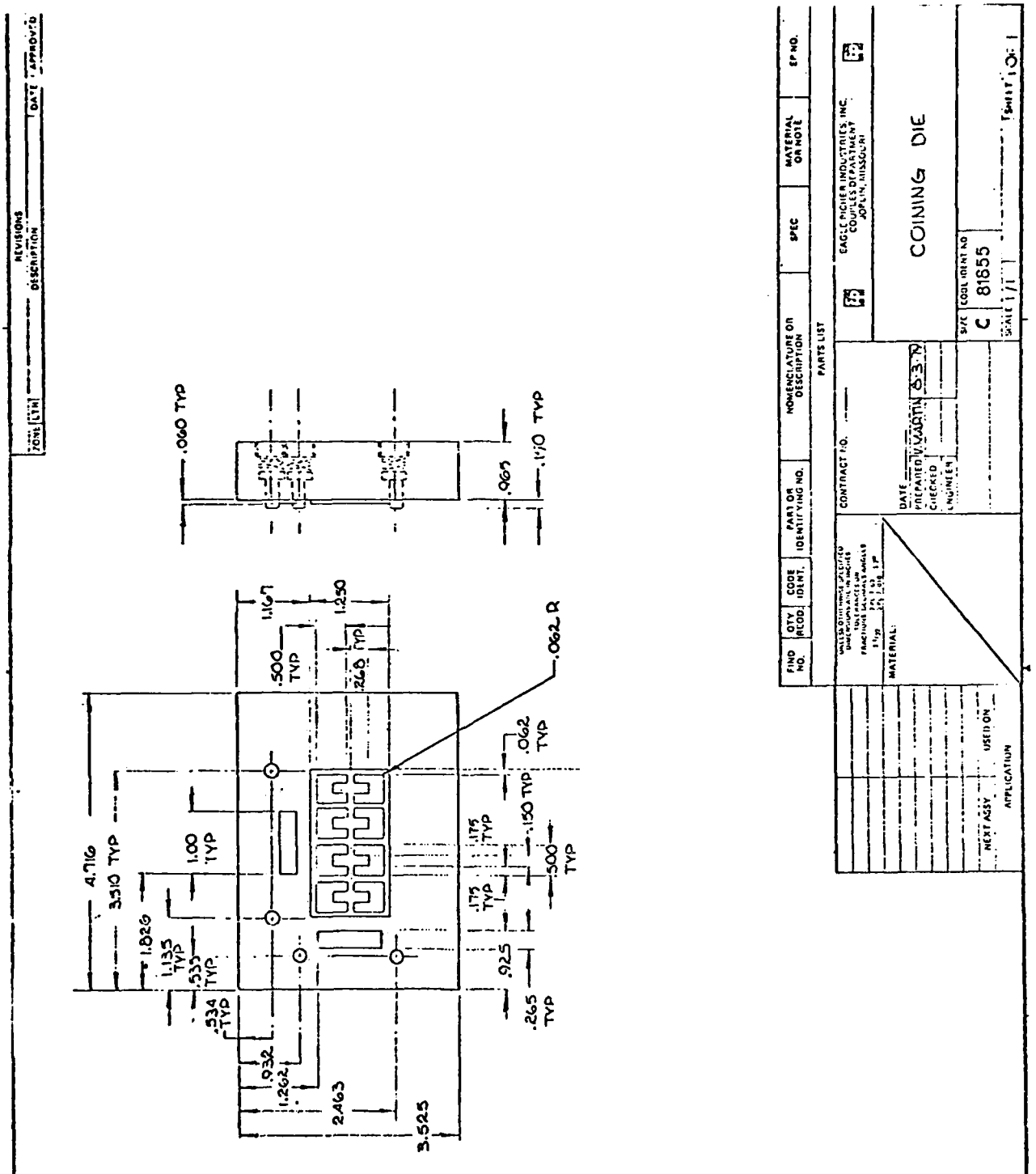

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