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IMPROVED CATHODE SYSTEMS FOR HIGH-ENERGY PRIMARY BATTERIES

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P. O. Box 309
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Contract No. F19628-67-C-0387

Project No. 8659
Task No. 865904
Work Unit No. 86590401

FINAL REPORT

1 July 1968 - 30 June 1969
October 15, 1969

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Contact Monitor: Richard Payne, Space Physics Laboratory

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UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS 01730

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I. ABSTRACT

The improvement of cathode performance in primary organic electrolyte batteries by conversion of the active material to an electronic semiconductor was investigated in this program. A series of n-type cadmium fluoride single crystals was prepared by a two-stage high-temperature doping process. Initial efforts to prepare n-type manganous fluoride by analogous procedures did not yield a conductive material. The cadmium fluoride crystals were characterized by the measurement of bulk and contact resistivities, using indium amalgam contacts. The crystal specimens were then examined electrochemically by cathodic discharge at constant current density in a lithium perchlorate - propylene carbonate electrolyte.

An electronic mechanism for the discharge of n-type cadmium fluoride was confirmed by the observation of cadmium deposition at the semiconductor/electrolyte interface. An undoped crystal was inactive when examined in the same electrode configuration. Two problems were encountered in the use of semiconducting cadmium fluoride as a cathode material: (1) passivation of the crystal surface, and (2) a requirement for careful preparation of the contact between the semiconductor and the external circuit. Recommendations for future work include investigation of the passivation process and means for its control, comparison of reaction rates for electronic and other discharge mechanisms, and continued efforts to prepare semiconducting transition metal halides.

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FIGURES (Continued)

II. INTRODUCTION

High-energy cathode materials that can be discharged rapidly in organic electrolytes are needed for the improvement of batteries utilizing lithium anodes. Transition metal fluorides and chlorides have been investigated for this purpose over a period of several years. Cadmium fluoride has received more recent attention.(1,2) In their usual forms, these solids have low electrical conductivities; the discharge process within a typical porous electrode structure apparently involves dissolution of the metal ion and its transport through the solution, followed by charge transfer at the surface of an inert current collector such as carbon. In this program, electronic conduction was introduced into the solid halide phase to provide an additional discharge mechanism and a corresponding improvement of cathode performance.

The first phase of the program was a study of _n_-type cadmium fluoride, for which preparation methods were available.(3,4) The second phase was an effort to prepare and evaluate a new semiconducting system from a selected transition metal fluoride or chloride. Evidence in support of the electronic reduction mechanism was obtained with powdered cadmium fluoride cathodes during the initial contract year.(1) In the second year, covered by this report, the cadmium fluoride study was extended, using single-crystal electrodes, and the preparation of _n_-type manganous fluoride by analogous doping methods was explored.

III. EXPERIMENTAL

The experimental activities consisted of: (1) materials preparation, including the growth of doped single crystals of cadmium fluoride and manganous fluoride, (2) bulk and contact resistivity measurements on the doped cathode materials, and (3) determination of constant-current discharge curves for single-crystal cadmium fluoride electrodes in a lithium perchlorate - propylene carbonate electrolyte. Experimental details are given below.

A. MATERIALS

1. High-Purity Chemicals

Preparation of the 1 M $LiClO_4$ solution in propylene carbonate from purified materials was described in the first scientific report on this program.(1) Argon used in distillation of the solvent was > 99.99% pure. The working anode and reference electrode were of solid lithium, 99.97% pure, obtained from Foote Mineral Co.

2. Single Crystals

The single crystals used in this work were prepared at the North American Rockwell Science Center.

a. Cadmium Fluoride

High-purity cadmium fluoride was obtained in powder form from the Chemical Products Plant of the General Electric Co. in Cleveland, Ohio. Starting material from this source had been used successfully in several earlier investigations of rare earth-doped cadmium fluoride.(3,5) Before crystal growth was attempted, the starting material was dried in anhydrous hydrogen fluoride at 400 to 600°C for a period of 12 to 24 hr. This procedure also converted any oxide that might have been present to the fluoride.

A series of cadmium fluoride crystals containing yttrium fluoride at concentrations ranging from 0.01 to 1 mole % was prepared by the Bridgman closed crucible method.(6) An undoped crystal was grown in the same way. (Initial growth attempts were made by the Czochralski crystal pulling technique,(6) but this method was discontinued because of nonuniform diameter growth.) The detailed procedure with the Bridgman method was as follows. The dried material was placed in an iridium crucible under helium, heated by induction until it was completely melted, and homogenized if a dopant was present. No yellow coloration was noted at any time during these steps until the cadmium fluoride was in the molten state; the starting material was thus relatively pure. The melt was then quenched and the resulting solid crushed and placed in a closed graphite crucible which had previously been baked out at 1200°C under vacuum for 1 to 4 hr. The crucible was lowered through an induction heating furnace using the Bridgman technique at a rate of 0.4 in./hr while rotating at 3 to 8 rpm. In general, the crystals were of good quality, transparent, and free of strain, with weights ranging from 20 to 30 g.

The doped crystals were cut perpendicular to the growth axis with a thin-sectioning saw into slices approximately 1 mm thick, using a kerosene-carborundum slurry as a cutting medium. The slices were washed in benzene, polished on an abrasive stone, etched in 1:1 hydrochloric acid, and sealed into evacuated quartz or Pyrex tubes, along with small pieces of cadmium metal. Heating for several minutes at 500°C produced the blue coloration characteristic of semiconducting cadmium fluoride.(7) The colored specimens were re-etched in hydrochloric acid to remove the undoped layer which was known to form on the surface during cadmium exposure. Further treatments were applied, as indicated in Section III-B, to produce the desired electrical contacts.

b. Manganous Fluoride

Manganous fluoride crystals doped with scandium, yttrium, and lutetium fluorides were grown by a similar procedure from starting material supplied by Electronic Space Products, Inc. of Los Angeles. The nominal dopant concentrations were 0.1 and 1 mole % Sc(III), 0.1 mole % Y(III), and 0.1 mole % Lu(III). The preparation containing 1 mole % Sc(III) was extensively cracked, and some similar difficulty was encountered with the lutetium-doped material. Good crystals were obtained in the other cases. Initial efforts to prepare a semiconducting manganous fluoride were made by treating crystal fragments containing 0.1 mole % Sc(III) with lithium or sodium vapor. Exposure conditions were varied from 15 min at 250°C to 1 hr at 500°C. Appreciable conductivity has not yet been produced in the manganese system.

B. SOLID-STATE MEASUREMENTS

1. Cadmium Fluoride

The four-terminal dc technique illustrated in Figure 1 was used to determine both bulk and contact resistivities of the cadmium fluoride crystals. Constant current densities ranging from 0.05 to 35 ma/cm^2 were passed between the ends of the crystal through terminals F and G by means of a 45-volt battery and a dropping series resistor. Connections from the amalgam contacts to the external circuit were made with the assistance of a four-element micromanipulator assembly. Potential differences between the various contacts were determined with a Leeds & Northrup K-3 potentiometer.

The bulk resistivity, ρ, was calculated from the equation

$$\rho = \frac{E_{H-I}}{E_a} \cdot R_s \cdot \frac{bc}{d} , \qquad (1)$$

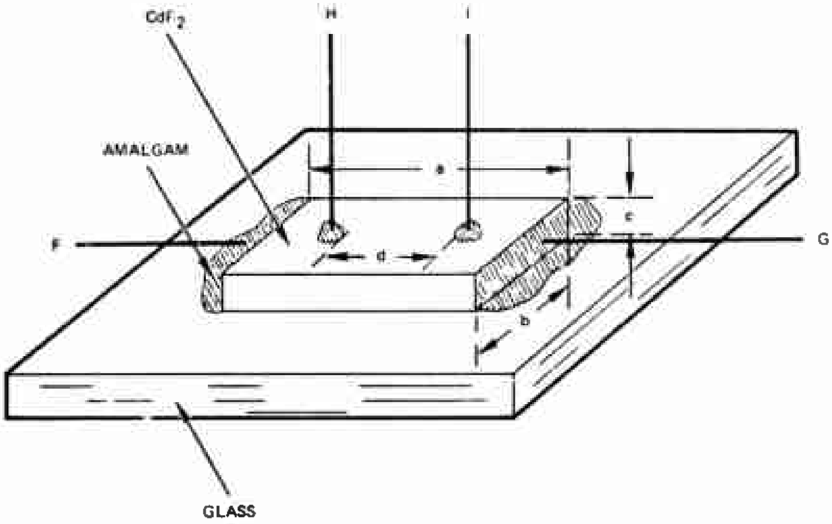

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Figure 1. Arrangement for Four-Terminal Resistivity Measurements

where E_{H-I} represents the potential difference between the probes at terminals H and I, E_s is the potential drop across a standard resistor, R_s, in series with the crystal, and b, c, and d are the dimensions indicated in Figure 1. With this arrangement, the bulk resistivity measurement was not ordinarily influenced by the relatively large potential drops across the current-carrying boundaries. Interference with the potential measurement between the probes which was noted occasionally at very low or zero current density may have been due to thermal effects. Under favorable conditions, however, the least accurate quantity in equation 1 was the interprobe spacing, d, which was known to about 20%. The contact resistances were examined at the same current densities by switching the potentiometer to positions F-H and I-G.

Metal contacts consisting of indium (applied by fusion), indium amalgam, and a low-melting indium solder* were investigated in preliminary experiments. A 50 wt % indium amalgam proved more satisfactory than the other materials, both mechanically and electrically. The amalgam was therefore used to obtain the detailed data that are given in this report. Acid-etched cadmium fluoride surfaces produced poor contacts. Further cleaning with organic solvents, including methanol and carbon tetrachloride, was tried, with little success, but benzene gave more satisfactory results. The amalgam contacts usually improved on standing overnight, probably due to the gradual penetration of crevices.

2. Manganous Fluoride

All of the manganous fluoride crystals had resistances greater than 10^9 ohms. The small sizea and irregular shapes of some of the chemically-treated specimens prevented effective use of the four-terminal technique.

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*50% In, 50% Sn, m.p. 116°C, from Electronic Space Products, Inc.

Dimensions were of the order of 2 to 5 mm. The total crystal resistance was obtained by a two-terminal measurement, in which the current through the crystal was evaluated from the ohmic drop measured across a comparatively small series resistance of 10^4 to 10^5 ohms. The crystal resistance, which was essentially that of the entire circuit, was then available from this current and the known battery voltage. Contact resistances are thus included in the data reported for manganous fluoride.

C. ELECTROCHEMICAL MEASUREMENTS

Instrumentation for the recording of potential-time curves at constant current and for estimation of the ohmic drop correction was described previously.(1)

The modified electrochemical cell used with the single-crystal cathodes is illustrated in Figure 2. The first crystal electrodes (Runs 1 and 3) were constructed in a polystyrene frame so that a flat surface, cut perpendicular to the growth axis, was exposed to the electrolyte. This mounting proved to be mechanically unstable; it was replaced in subsequent runs with the epoxy type shown in Figure 3. The exposed area was then on a freshly-cleaved and slightly uneven surface, essentially parallel to the growth axis. The detailed electrochemical sequences are indicated in Section IV.

The solution resistance between the cathode and reference electrodes was not directly measurable by the pulse technique used previously for carbon paste electrodes(1) because of the blocking space-charge capacitance in the semiconductor crystal. Pulse measurements in which a copper electrode of similar size was substituted for the crystal indicated negligible solution ohmic drop at the current densities employed in the discharge measurements.

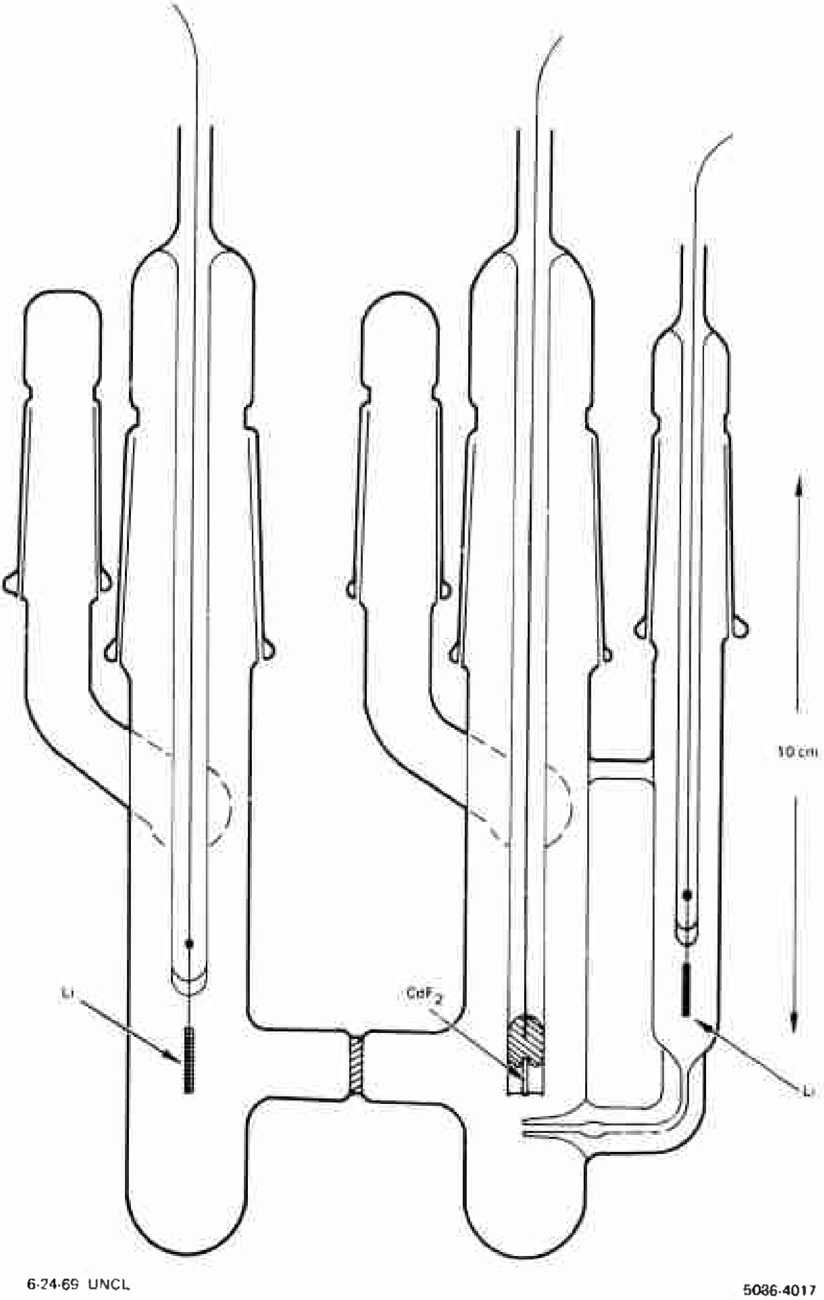

Figure 2. Electrochemical Cell

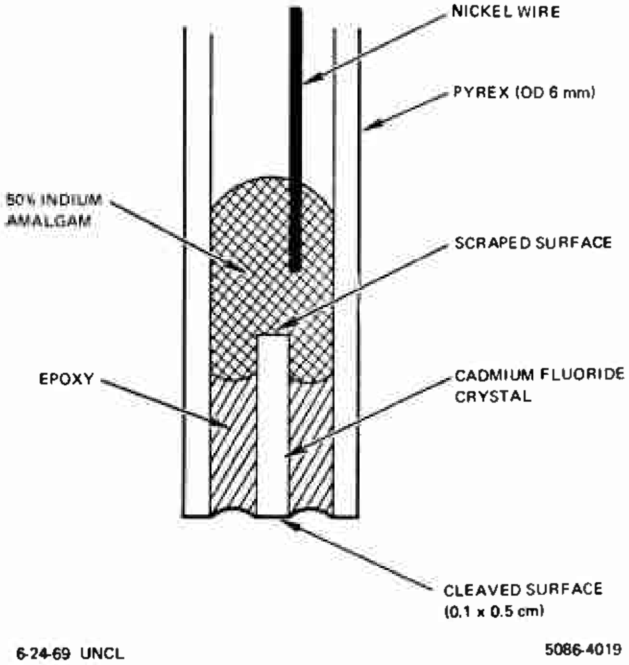

Figure 3. Single-Crystal Electrode

IV. RESULTS AND DISCUSSION

The results of the program are discussed in this section, with attention to three requirements for implementation of the semiconductor approach to battery cathode improvement. These requirements are: (1) a means for conversion of the selected oxidizer to a semiconductor, (2) formation of a low-resistance contact from the semiconductor to the external circuit, and (3) a rapid, unhindered electrochemical discharge process at the electrolyte interface. This investigation dealt with each of these requirements for the cadmium fluoride system; it will be seen that some further study of the discharge process is needed in this case. For the transition metal halides, the production of semiconducting materials has been explored on a preliminary basis but has not yet been accomplished.

A. FORMATION OF SEMICONDUCTING HALIDES

1. General Guidelines*

Most, if not all, of the halides of interest in this program are insulators in the pure state. Cadmium fluoride, for example, has an energy gap of 6 ev(7) and a room temperature resistivity of approximately 10^7 ohm-cm.(5) A dopant that will act as a simple donor or acceptor in such a system is not easily found. The formation of n-type cadmium fluoride by the two-stage process of Prener and Kingsley involves:(3)

1) Substitution of a trivalent cation for Cd^{++} in the CdF_2 lattice, with the consequent formation of an interstitial F^-
2) Migration of interstitial F^- at high temperature to the outer surface of the cryatal where a reaction occurs with cadmium atoms: $2F^- + Cd^\circ \rightarrow CdF_2 + 2e$

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*Notations used in thia aection are: MX_2 for the halide of a divalent metal, M^{++} for the corresponding hoat crystal cation, X^- for the host anicn, F^- for fluoride ion. The other chemical symbols are conventional.

A thin layer of undoped cadmium fluoride forms on the surface, and an equivalent number of electrons are released to the interior of the crystal. Optical spectra show that these extra electrons do not reduce the trivalent ions when a conducting system is obtained but instead remain in a delocalized state.(4) ESR spectra indicate, however, that some interaction between the extra electron and the dopant ion may occur.(5) Stabilization of the conducting system apparently depends on the presence of a number of nearest cation neighbors surrounding each trivalent ion. Thus, in cadmium fluoride, which has a face-centered cubic lattice, each substituent cation is surrounded by 12 nearest Cd^{++} neighbors at a distance of 3.81 Å. This environment facilitates an exchange of the type

$$Cd^{++} + Cd^{+} \rightarrow Cd^{+} + Cd^{++}$$

involving the cadmium 5s state. The resulting "impurity" band is believed to be responsible for high electron mobility and strong infrared absorption by the semiconductor.(4)

From this knowledge of the cadmium fluoride system, certain criteria for the analogous formation of other semiconducting halides of the type MX_2 may be specified. Other doping methods are not to be excluded, but the Prener and Kingsley approach, outlined above, has been the one applied to date in this investigation. Requirements for successful doping by that method may be summarized as follows:

1) A trivalent cation of size near that of M^{++} or smaller should be available to substitute in the crystal lattice.
2) The impurity cation should be stable in the +3 oxidation state. It should not be reduced by M° or oxidized by M^{++}.

3) The impurity ion should not coordinate with X^- to an extent that interferes with its mobility at high temperature.

4) The lattice of the host crystal should have enough open space to form X^- interstitials.

5) The cation lattice should be capable of stabilizing the extra electrons that compensate for lost X^-. A large number of M^{++} neighbors should surround each cation site with a symmetry favoring electron exchange. However, deep trapping of electrons on the host cations should be avoided.

For the transition metal halides, Conditions 1 and 2 are likely to be met by dopant cations such as Sc^{+++} and Al^{+++}. Condition 3 suggests the choice of F^-, rather than Cl^-, as the crystal anion. Conditions 4 and 5 are dependent on crystal structure and on the electron affinities of the host and impurity cations. Cupric ion in the role of M^{++} may trap electrons too strongly, with a resultant low carrier mobility, but the extent of this problem has not been determined. The other cations of interest have no pronounced tendency to form M^+.

Some crystal properties of cadmium fluoride and a group of transition metal halides which pertain to Conditions 4 and 5 are given in Table 1. In arriving at the last column of this Table, it was assumed that a prospect for interstitial anions exists when the free volume per molecular unit, MX_2, exceeds the volume of the anion computed from its crystal radius. This criterion is easily met for CdF_2, MnF_2, and CuF_2. Marginal cases are found in CoF_2 and NiF_2, and none of the chlorides appears likely to form interstitials. The fulfillment of Condition 5, for electron stabilization, is more difficult

TABLE 1

CRYSTAL PROPERTIES OF CATHODE MATERIALS

Cathode Material (MX_2)	Theoretical Energy Density[a] (whr/lb)	Crystal System	Crystal Density (g/cc)	Crystal Volume per Molecule (Å^3)	Single Ion Volumes[b]		Interstitial Volume per Molecule (Å^3)	Prospects for Interstitial Anions
					Cation (Å^3)	Anion (Å^3)		
CdF_2	599	Cubic	6.386(8)	39.10	3.82	10.54	14.20	+
MnF_2	495	Tetragonal	3.925(9)	39.31	2.14	10.54	16.09	+
CoF_2	634	Tetragonal	4.592(9)	35.05	2.31	10.54	11.66	?
NiF_2	620	Tetragonal	4.814(9)	33.35	1.37	10.54	10.90	?
CuF_2	744	Monoclinic	4.91(10)	45.5	0.77[c]	10.54	23.6	+
$MnCl_2$	294	Hexagonal	2.977(11)	70.19	2.14	24.8	16.5	-
$CoCl_2$	433	Hexagonal	3.356(11)	64.24	2.31	24.8	12.3	-
$NiCl_2$	437	Hexagonal	3.537(11)	60.34	1.37	24.8	9.8	-
$CuCl_2$	501	Monoclinic	3.054(11)	73.09	0.77[c]	24.8	22.7	-

[a] For the cell reaction: $2Li + MX_2 \rightarrow M + 2LiX$

[b] Based on Pauling crystal radii unless otherwise noted

[c] Based on cupric ion radius in CuF_2

to predict. In the tetragonal MnF_2 crystal, for example, each cation site has 8 Mn^{++} neighbors at a distance of 3.82 Å and 2 at 3.31 Å. To compare extra electron stabilization in this slightly flattened structure with that in the nearly-spherical cation environment of CdF_2, one should consider the sizes and shapes of the orbitals involved, whether 3d or 4s in the case of MnF_2, and their interactions with the anion lattice, as well as the electron affinities of host and impurity cations. The related question of intrinsic conduction in transition metal halides, oxides, and sulfides was treated by Morin, who correlated the wide-ranging electrical properties with orbital overlap integrals.(12) The scope of the present program did not provide for a quantitative theoretical analysis of the doping problem.

2. Initial Results for Manganous Fluoride

The results of initial experimental efforts to prepare n-type manganous fluoride by the Prener and Kingsley approach are summarized in Table 2. It was noted previously that this compound should be capable of forming F^- interstitials. As a battery cathode material, manganous fluoride offers a theoretical energy density of 495 whr/lb, compared to 399 whr/lb for cadmium fluoride. Alkali metal vapors were used in the reduction stage, rather than manganese, because the vapor pressure of the latter is too low for an effective conversion process. Pyrex containers reacted with the alkali metals to some extent, but quartz tubes were found to be satisfactory. During the more intensive exposures, the crystals became coated with a dark layer, presumably of manganese metal. When this layer was etched away, however, the measured crystal resistance remained higher than 10^9 ohms in all cases. The slightly lower values observed after 1 hr in sodium vapor at 500°C may be significant. Further work on the doping of manganous fluoride by this approach is recommended.

TABLE 2

EFFECT OF ALKALI METAL VAPORS ON SCANDIUM-DOPED MANGANOUS FLUORIDE[a]

Metal Vapor Exposure			Crystal Resistance[b] (ohms)	Notes
Metal	Temperature (°C)	Time (min)		
Sodium	250	15	2.2×10^{10}	
	500	65	1.2×10^{10}	Successive exposures of 15, 20, and 30 min
	500	60	6.5×10^{9}	New contacts
			3.1×10^{9}	Contacts in place 48 hr
Lithium	250	15	2.5×10^{10}	
	500	65	2.4×10^{10}	Successive exposures of 15, 20, and 30 min
	500	60	1.8×10^{10}	

[a] 0.1 Mole % Sc(III)

[b] 2-Terminal method; includes interfacial resistance

Some difficulties were encountered earlier in the preparation of *n*-type cadmium fluoride from polycrystalline material.(1) The blue semiconductor was easily produced from the yttrium-doped single crystals, however, as indicated in the next section.

B. RESISTIVITIES OF CADMIUM FLUORIDE CRYSTALS

The bulk resistivity of the cathode material was needed to establish its influence on the electrochemical discharge mechanism. It is also apparent that the contact resistance at the current collector interface must be minimized, if the performance capabilities of a doped cathode system are to be fully realized. The bulk and surface resistance terms were resolved experimentally by the four-terminal measurements on the cadmium fluoride crystals, with the results indicated in the following paragraphs.

1. Bulk Resistivity

Bulk resistivities for the series of yttrium-doped cadmium fluoride crystals are included in Table 3. Detailed data for six crystals are given in the Appendix (Table 6). The observed resistivities are consistent with the 1 ohm-cm magnitude reported for a variety of similarly-doped cadmium fluoride systems containing 0.1 mole % rare earth or yttrium ions.(4)

In the present work, the dependence of the bulk resistivity, ρ, on dopant concentration appears to have been obscured somewhat by other factors, possibly nonuniform thermal treatment during crystal growth or cadmium exposure. A ten-fold variation of ρ was nevertheless observed within this series. The highest resistivity, 3.2 ohm-cm, was obtained by lowering the cadmium exposure temperature from 500 to 300°C.

TABLE 3

CHARACTERISTICS OF CADMIUM FLUORIDE CRYSTALS

Crystal Specimen	Mole % Y(III)	Cadmium Treatment Temperature[a] (°C)	Resistivity[b] (ohm-cm)	Electrode Area[c] (cm^2)	Electro-chemical Run	Comments
6-1	1	500	0.44	-	-	
6-2		500	0.44	0.050	2	
6-3		500	0.58	0.077	3	Etched surface exposed; incomplete run
2-4	0.1	500	1.2	-	-	
4-1	0.05	500	0.30	-	-	
4-2		500	0.34	~ 0.25	1	Etched surface exposed; incomplete run
4-3		500	0.27	-	-	
3-1	0.01	500	1.0	-	-	
3-2		500	0.74	-	-	
3-3		500	0.68	0.049	4, 7	Re-cleaved after Run 4
5-1	0.01	500	1.3	-	-	
5-2		None	2.2	-	-	Pale blue and conductive without cadmium treatment[d]
5-3		300 (3 hr)	3.2	0.033	6	
1-1	0	None	$>3 \times 10^6$	0.05	5	

[a] Exposed to cadmium vapor several minutes unless noted

[b] Average of four or more measurements made at two or more current densities

[c] Cleaved surface exposed to electrolyte unless noted

[d] Possibly due to reduction of cadmium oxide during crystal growth

2. Contact Resistivity

The contact resistivity, reported in Table 6, is defined as the ratio of interfacial potential drop to current density and may be expressed as ohm-cm^2. This "resistance" does not always behave as a simple ohmic circuit element at metal-semiconductor contacts. In idealized systems, rectification effects are predictable from the work functions of the two solids. In real systems, however, the work function contributions are usually obscured by those of barriers consisting of adsorbed materials, surface impurities, and the like. Such was the case in the present work.

The results of the contact resistance investigation are summarized graphically in Figures 4 and 5. The symbols F and G denote the potentials of the respective interfaces, measured against the nearest probe. Two tendencies were apparent from the outset with the chemically-cleaned surfaces: (1) rectification occurred with a directional characteristic opposing cathodic discharge, and (2) the two ends of the crystal responded in a similar manner with the same current polarity; it was not difficult to produce a fairly uniform surface, although the interfacial resistivity was high enough to cause a serious power loss in an electrochemical cell. These features are evident in Figure 4 at 0.01 mole % yttrium. When this crystal was freshly cleaved, the contact improved significantly and began to approach ohmic behavior. Finally, as shown in Figure 5, an ohmic contact was achieved on a freshly-cleaved 1 mole % crystal. The contact resistivity then dropped from the range of 10 to 1000 ohm-cm^2 to a consiatent 0.36 ohm-cm^2, independent of the magnitude or direction of the current. These results point to surface contamination, rather than intrinsic work function differences, as the principal cause of the contact resistance.

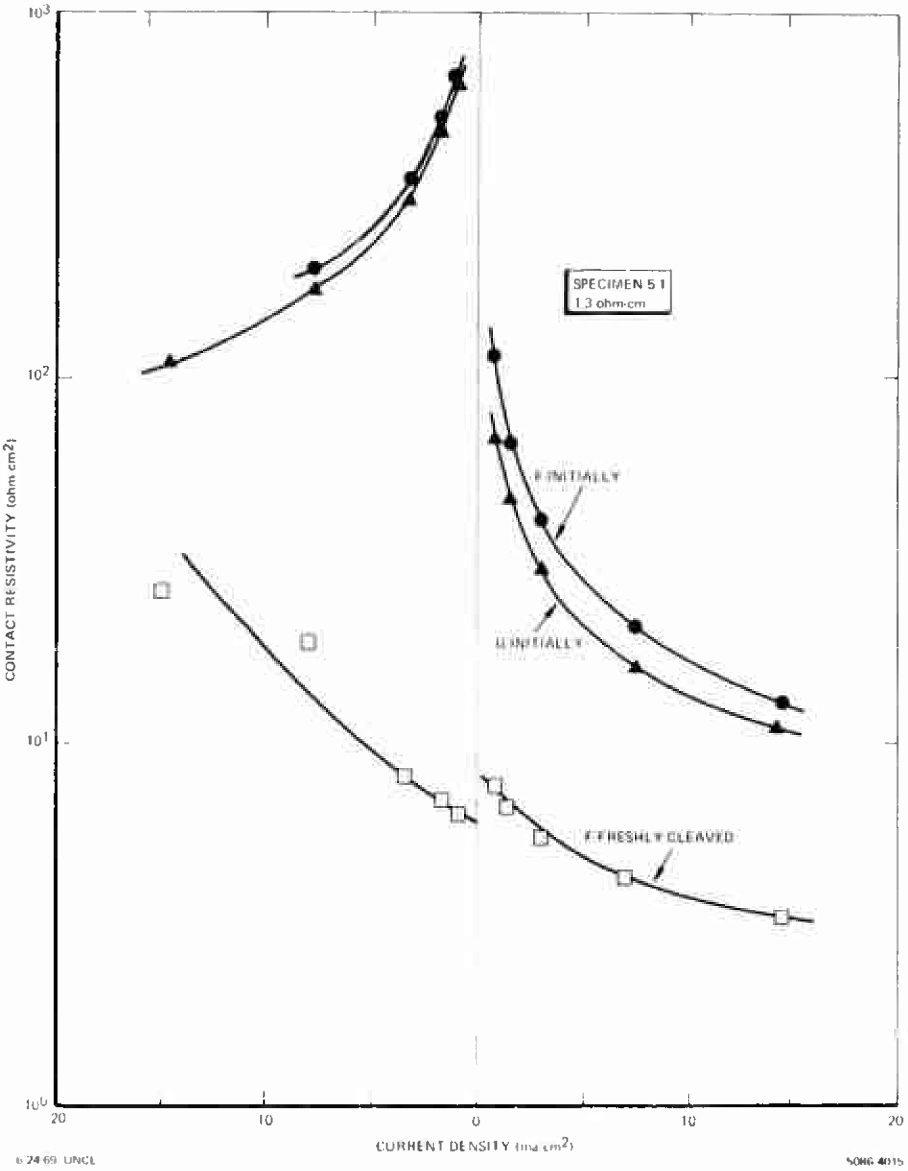

Figure 4. Contact Resistivities of Cadmium Fluoride Containing 0.01 Mole Percent Yttrium

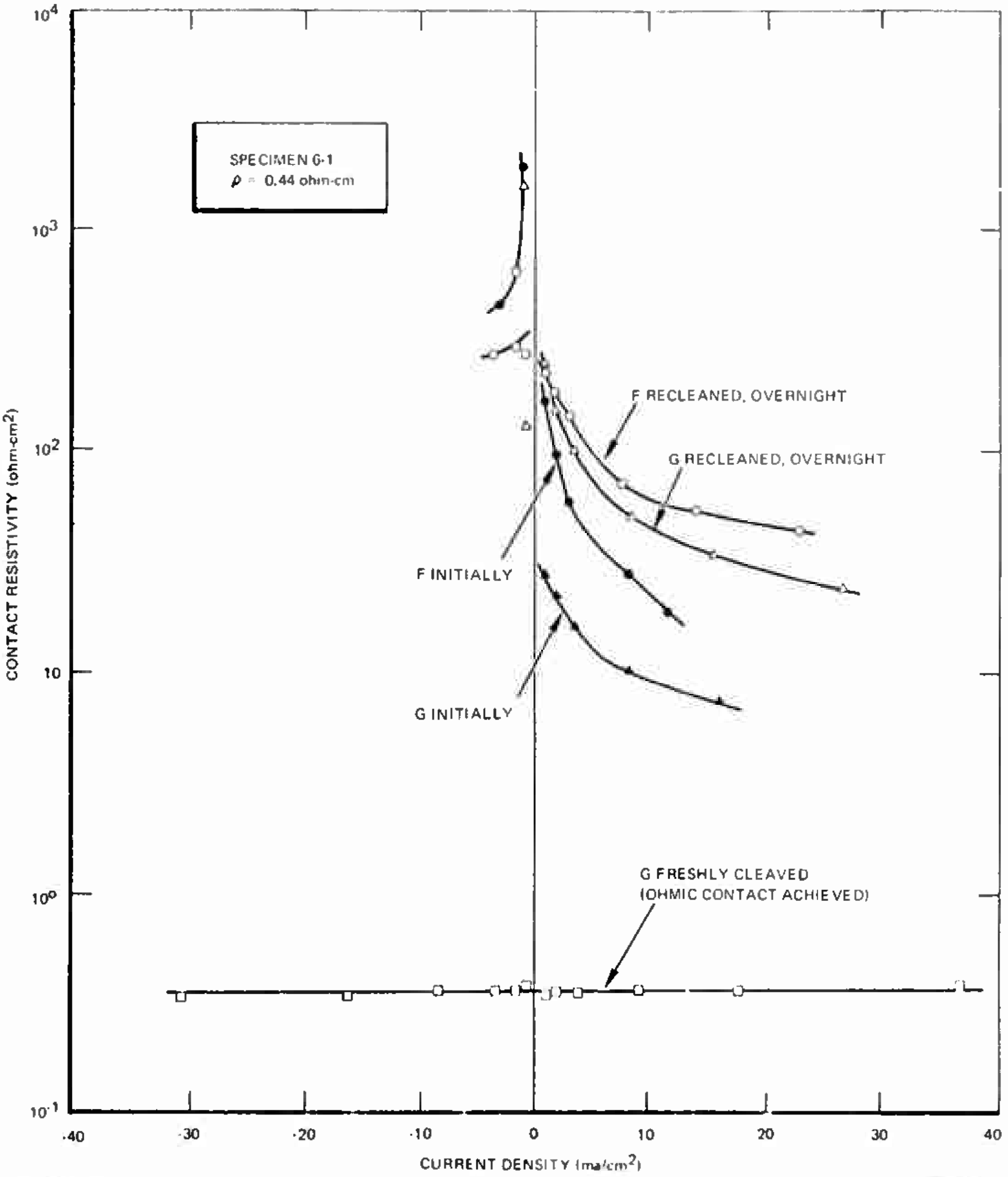

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Figure 5. Contact Resistivities of Cadmium Fluoride Containing 1 Mole Percent Yttrium

C. CATHODIC BEHAVIOR OF N-TYPE CADMIUM FLUORIDE CRYSTALS

Chemical and physical characteristics of the crystal specimens used as electrodes are given in Table 3. Detailed electrochemical sequences and the corresponding data are recorded in Table 4. Table 5 provides a summary of the results. Several features of the crystal electrode behavior are discussed below.

1. Open-Circuit Potential and Initial Polarization

The calculated equilibrium potential for the cell $Li/LiF(s)/CdF_2(s)/Cd$ is 2.70 v. Initial open-circuit potentials determined experimentally on the doped crystals were 2.4 to 2.6 v vs Li/Li^+(1 M) while a value of only 1.73 v was recorded on the undoped material.

Preliminary discharges of 1 min duration were made on each of the doped crystals at 0.1 and 0.2 ma/cm^2, to compare initial polarizations and to establish a suitable current density level for more prolonged discharge experiments. The preliminary curves for 0.68 and 3.2 ohm-cm crystals are shown in Figures 6 and 7, respectively. The initial polarizations were not excessive under these conditions, and the cathodes recovered within several minutes on open circuit to new potentials approaching the theoretical value. In these measurements on crystals with good electronic conduction, the shapes of the preliminary discharge curves were more responsive to a two-fold increase in current density than to a five-fold increase in bulk resistivity.

In contrast, the undoped crystal (Run 5) failed to pass a current of 5 μa (0.1 ma/cm^2), even when 420 v was applied between the anode and cathode. The resistance of this crystal waa known, from the solid-state measurements, to be $> 3 \times 10^7$ ohms. Its behavior on attempted discharge was therefore not surprising. This result confirms the absence of an electronic or solid-state ionic reduction mechanism for undoped cadmium fluoride.

TABLE 4

ELECTROCHEMICAL DATA FOR CADMIUM FLUORIDE CRYSTALS

Run	Crystal Resistivity[a] (ohm-cm)	Procedure	Open-Circuit Potential[b] (volts)	Current Density (ma/cm^2)	Transitions		Notes
					Potential (volts)[b]	Time (min)	
1	0.34	Incomplete					Polystyrene crystal mounting unsatisfactory; cadmium deposition observed
2	0.44	1st preliminary discharge	2.43	0.1			
		2nd preliminary discharge	2.52	0.2			
		1st continuous discharge	2.54	0.1	1.08 0.68	15.4 22.1	Figure 8
		1 hr on open circuit, followed by 2nd continuous discharge	. 2	0.1	1.05 0.60	3.2 5.3	
		60 min on open circuit, followed by 3rd continuous discharge	2.25	0.1			Several short transitions, not well resolved
		Cathode exposed to water 5 min; 4th continuous discharge	2.42	0.1	1.05 0.76	109 139	Epoxy seal had softened slightly, exposing a larger area of crystal
3	0.58	Incomplete	2.55				Polystyrene mounting
4	0.68	1st preliminary discharge	2.50	0.1			
		2nd preliminary discharge	2.58	0.2			
		1st continuous discharge	2.60	0.1	1.04 0.72	32.0 35.9	Figure 9

TABLE 4 (Continued)

Run	Crystal Resistivity[a] (ohm-cm)	Procedure	Open-Circuit Potential[b] (volts)	Current Density (ma/cm^2)	Transitions		Notes
					Potential (volts)[b]	Time (min)	
4 (Cont)		16 min on open circuit, followed by 2nd continuous discharge	2.19	0.1			No inflections; potential dropped rapidly to zero (Figure 12)
		11 min on open circuit, followed by 3rd continuous discharge	2.16	0.1			No inflections; as above
		Cathode exposed to water 5 min; 4th continuous discharge	2.29	0.1	1.20 0.79	48.7 67.8	Epoxy seal remained firm; no evidence of electrolyte seepage (Figure 13)
7	0.68	1st preliminary discharge	2.60	0.1			Electrode from Run 4 was recleaved and used again (Figure 6)
		2nd preliminary discharge	2.72	0.2			Figure 7
		8 min on open circuit, followed by 1st continuous discharge	2.74	0.2	1.17	7.5	Earlier inflection at 1.48 v; no clear transition below 1.17 v (Figure 11)
		31 min on open circuit, 20 min charging at 0.2 ma/cm^2 followed by 2nd continuous discharge	2.60	0.2			Reached 1.0 v in 5 min; discharge curve resembled Figure 15
		8 min on open circuit, followed by 3rd continuous discharge	2.01	0.2			Rapid drop; no inflections

TABLE 4 (Continued)

Run	Crystal Resistivity[a] (ohm-cm)	Procedure	Open-Circuit Potential[b] (volts)	Current Density (ma/cm²)	Transitions		Notes
					Potential (volts)[b]	Time (min)	
7 (Cont)		6 min on open circuit; 13 min charging at 0.2 ma/cm², followed by 4th continuous discharge	2.64	0.2			Cathode potential rose to 8.7 v on charging; dropped immediately to 2.95 v when charging ceased (Figures 14 and 15)
		9 min on open circuit, followed by 5th continuous discharge	2.20	0.2			Sharp drop; no inflections
6	5.2	1st preliminary discharge	2.59	0.1			Figure 7
		2nd preliminary discharge	2.65	0.2			Figure 7
		1st continuous discharge	2.67	0.1	1.12 0.69	16.4 26.5	Figure 10
		17 min on open circuit, followed by 2nd continuous discharge	2.22	0.1	0.87 0.66	0.8 1.6	
		12 min on open circuit, followed by 3rd continuous discharge	2.17	0.1			Rapid drop; very minor inflections
		64 hr on open circuit; 4th continuous discharge	2.52	0.1	1.05	11.9	Some discharge capacity was recovered on long standing but seal was slightly softened
5	~5 x 10^6	Attempted discharge	1.78	Set for 0.1			Undoped crystal; power supply reverted to voltage-limiting condition with 420 v applied to cell

[a] Detailed characteristics of crystals are given in Table 3

[b] Measured vs Li/LiClO$_4$ (1 M)

TABLE 5

SUMMARY OF ELECTROCHEMICAL RESULTS FOR CADMIUM FLUORIDE

Run	Crystal Resistivity (ohm-cm)	Initial Open Circuit Potential[a] (volts)	Transitions[b]		Utilization Thickness (microns)	Energy Density[c] (whr/lb)
			Potential[a] (volts)	Time (min)		
2	0.44	2.43	1.08	15	0.11	250
			0.68	22	0.16	210
4	0.68	2.50	1.04	32	0.23	240
			0.72	36	0.26	230
			1.20[d]	49[d]	0.36	250
			0.79[d]	68[d]	0.50	220
7	0.68	2.60	1.17[e]	7.5[e]	0.11	240
6	3.2	2.59	1.12	16	0.12	220
			0.69	26	0.19	200
5	$> 3\times10^6$	1.78	-	-	-	-

[a] Measured vs $Li/LiClO_4$ (1M) before any discharge

[b] 1st continuous discharge, current density 0.1 ma/cm^2 unless noted

[c] Based on the utilized cadmium fluoride and the corresponding weight of lithium

[d] Following exposure of discharged crystal to water

[e] Current density 0.2 ma/cm^2

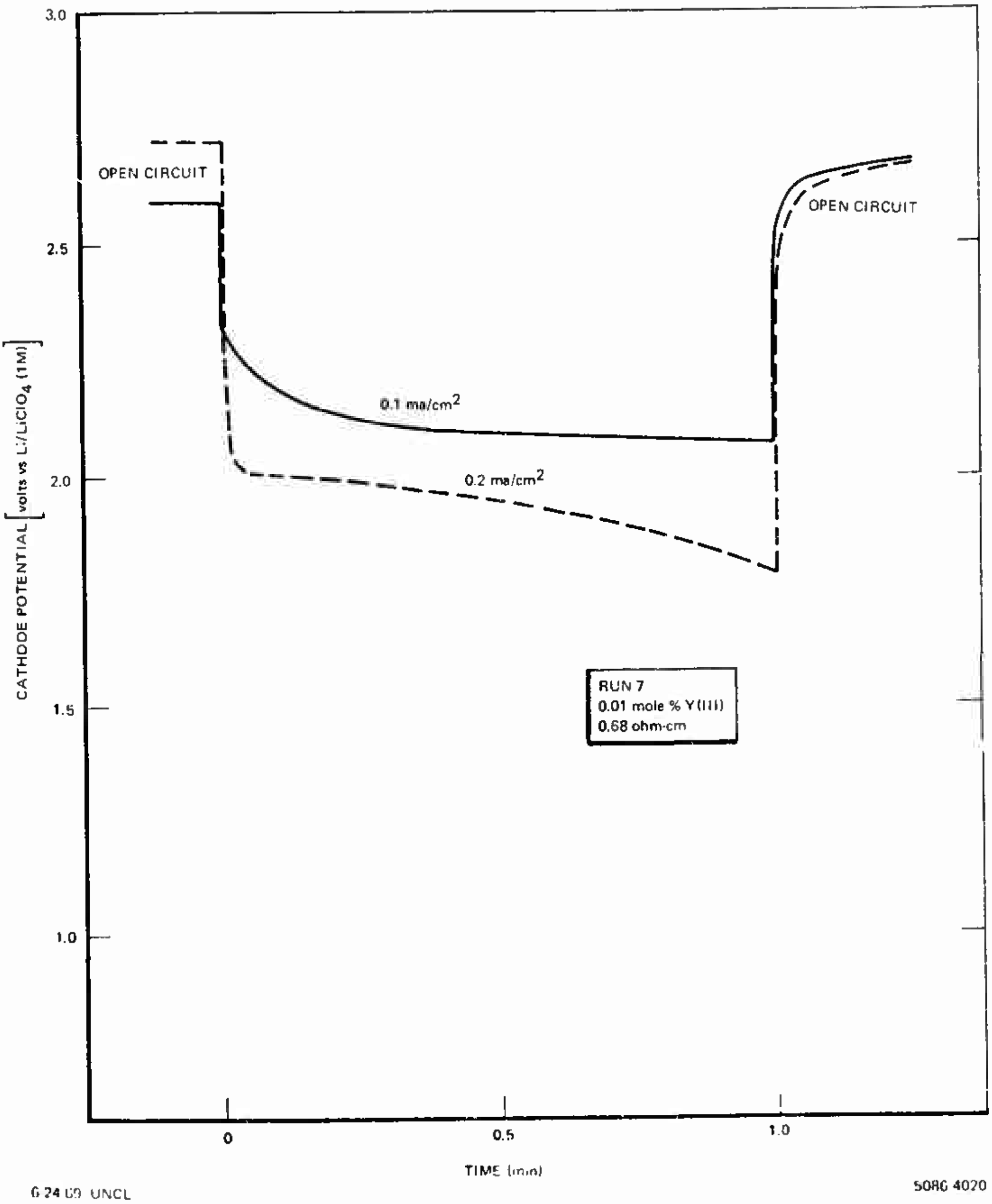

Figure 6. Preliminary Discharges of 0.68 ohm-cm Cadmium Fluoride Crystal

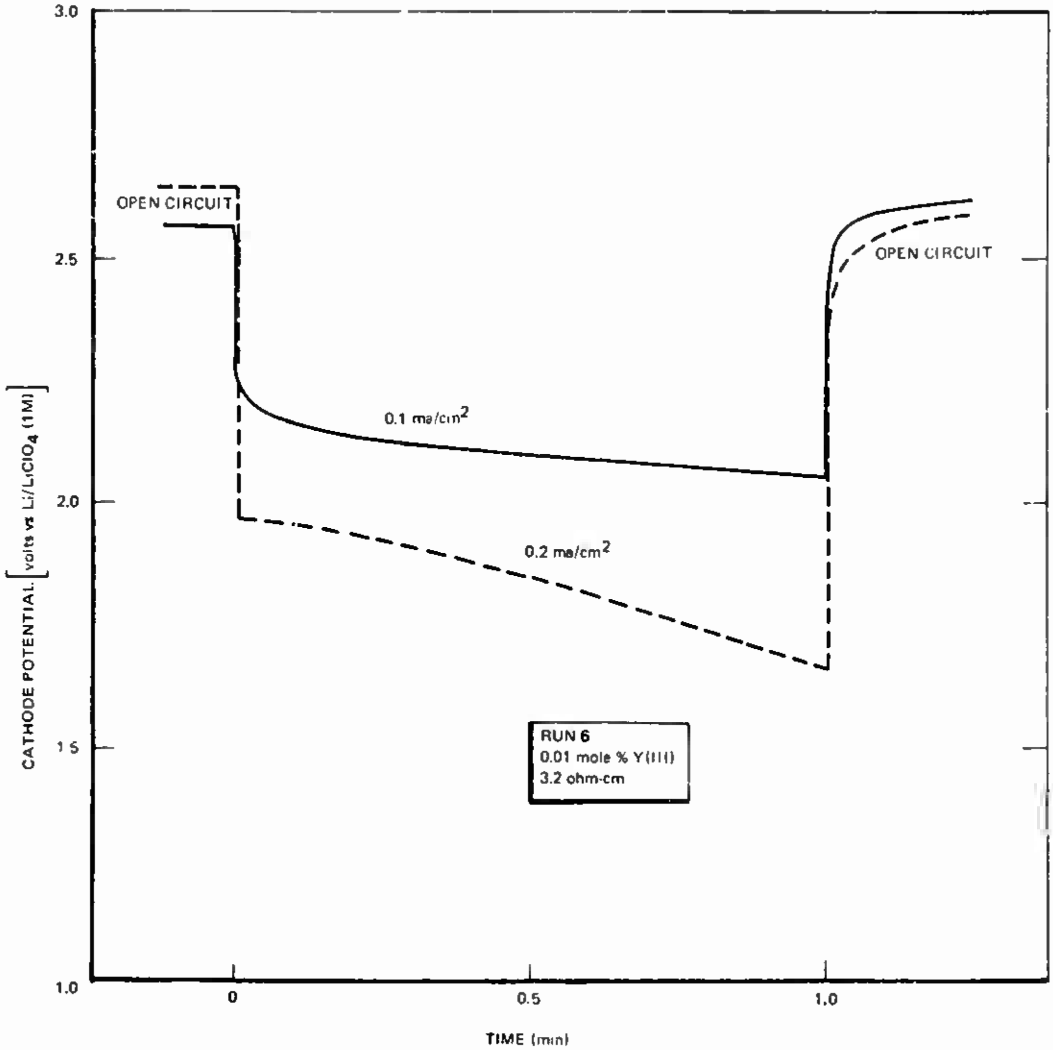

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Figure 7. Preliminary Discharges of 3.2 ohm-cm Cadmium Fluoride Crystal

2. Behavior on Prolonged Discharge

When cathodic reduction of a salt or oxide occurs by an electronic mechanism, the corresponding metal is deposited at the semiconductor/electrolyte boundary.(1) With a solid-state ionic mechanism, the metal forms at the boundary between the ionic crystal and the electronic current collector. A dark layer of cadmium metal became visible on the outside of the cadmium fluoride crystals when the discharge times were extended to several minutes. No change was observed at the mirror-like amalgam contact. Upon continued discharge, the cadmium deposit acquired a more metallic appearance. The discharged electrode was removed from the cell, washed in water, and dried. The dark layer showed high conductance on a dc ohmmeter. Thus, the electronic discharge mechanism was established for *n*-type cadmium fluoride.

The first continuous discharge curves for the doped crystals at 0.1 ma/cm^2 are shown in Figures 8, 9, and 10. A discharge curve for one of the same crystals, re-cleaved, at 0.2 ma/cm^2 is recorded in Figure 11. Two processes are indicated by inflections near 1.0 and 0.7 v. Both transitions are clearly visible in Figure 8 but are not as well resolved in the other cases. The equivalent thicknesses of cadmium fluoride utilized at the transition potentials, calculated under the assumption of 100% current efficiency, are given in Table 5. The energy densities were obtained by integration of the potential-time curves to the indicated transition points. The utilization thickness on a cleaved surface was 0.1 to 0.2 micron. Apparently, cathodic passivation of the crystal surface occurred when a layer of cadmium fluoride about 200 unit cells in thickness had been reduced. Following the initial discharge to 0.2 v (Figure 9)the cathode again recovered on open circuit to

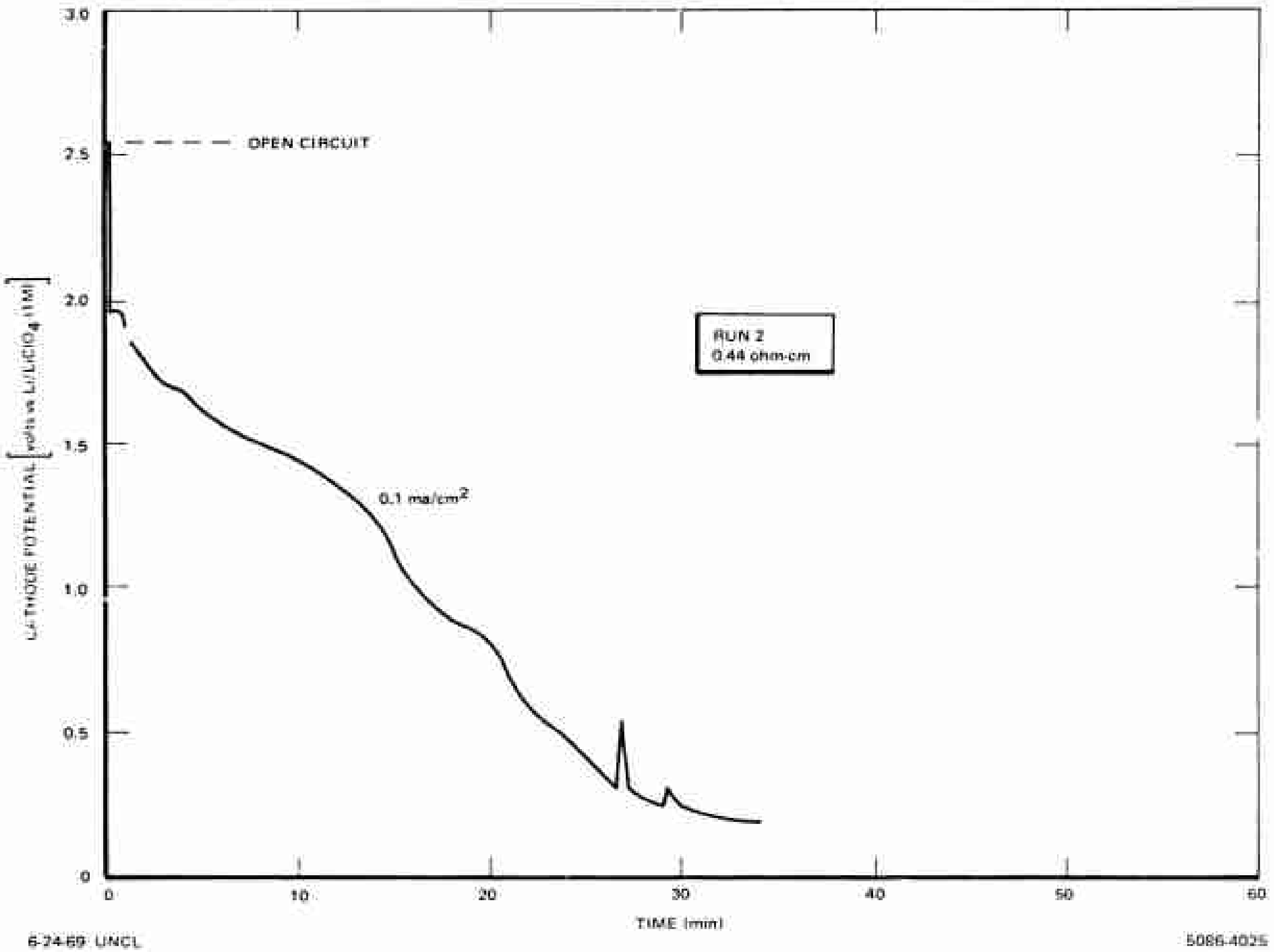

Figure 8. First Continuous Discharge of 0.44 ohm-cm Cadmium Fluoride Crystal at 0.1 ma/cm^2

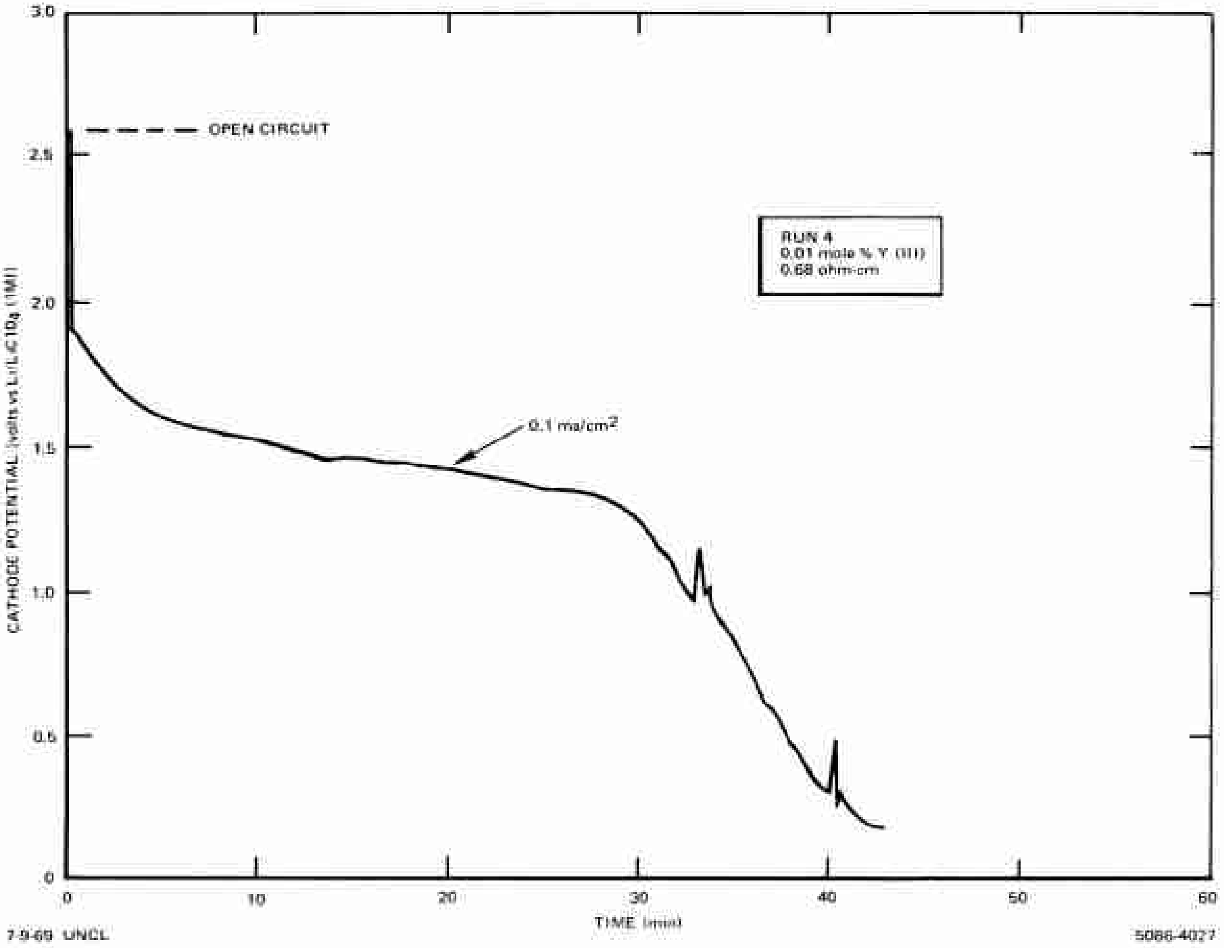

Figure 9. First Continuous Discharge of 0.68 ohm-cm Cadmium Fluoride Crystal at 0.1 ma/cm^2

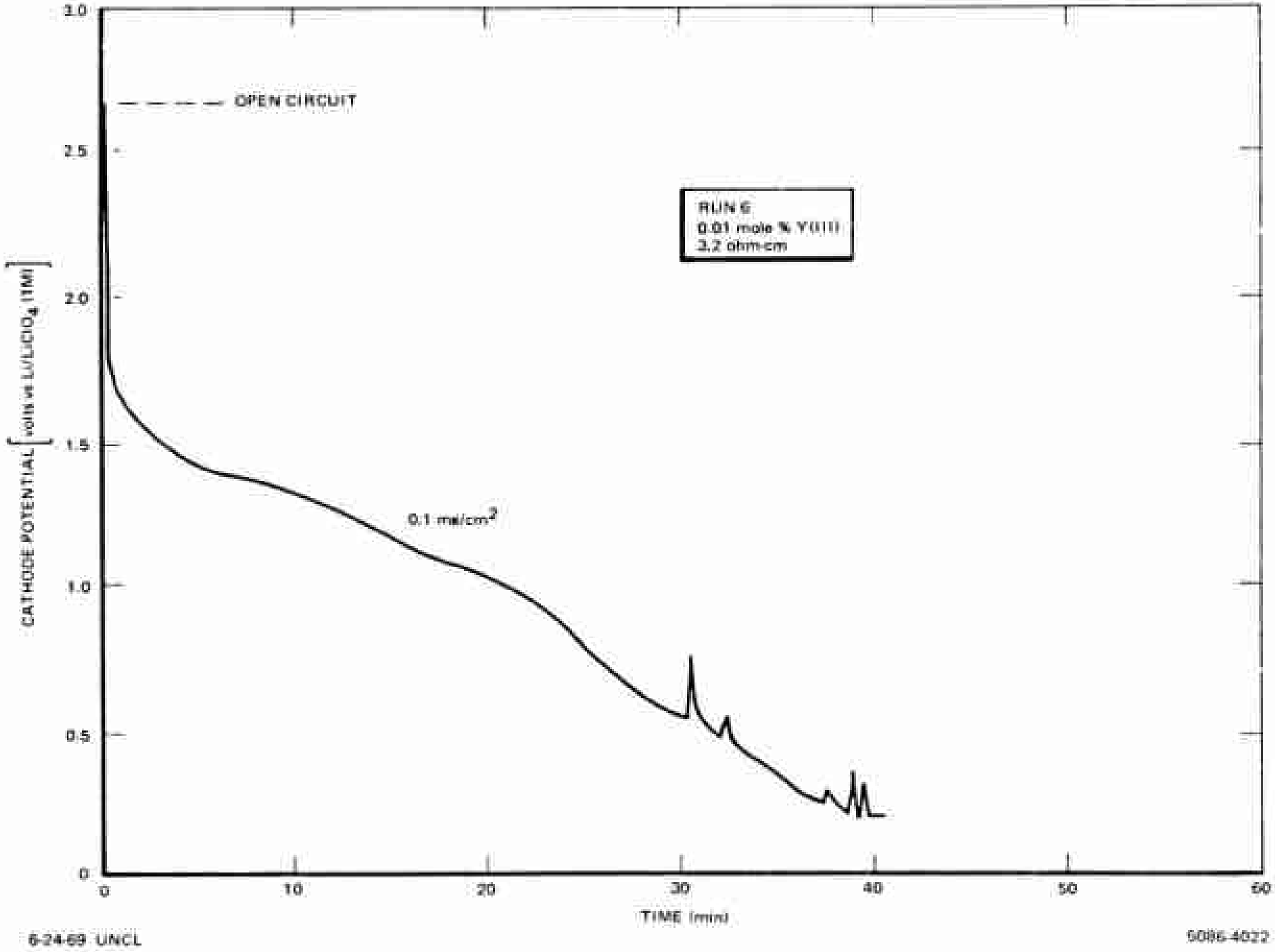

Figure 10. First Continuous Discharge of 3.2 ohm-cm Cadmium Fluoride Crystal at 0.1 ma/cm^2

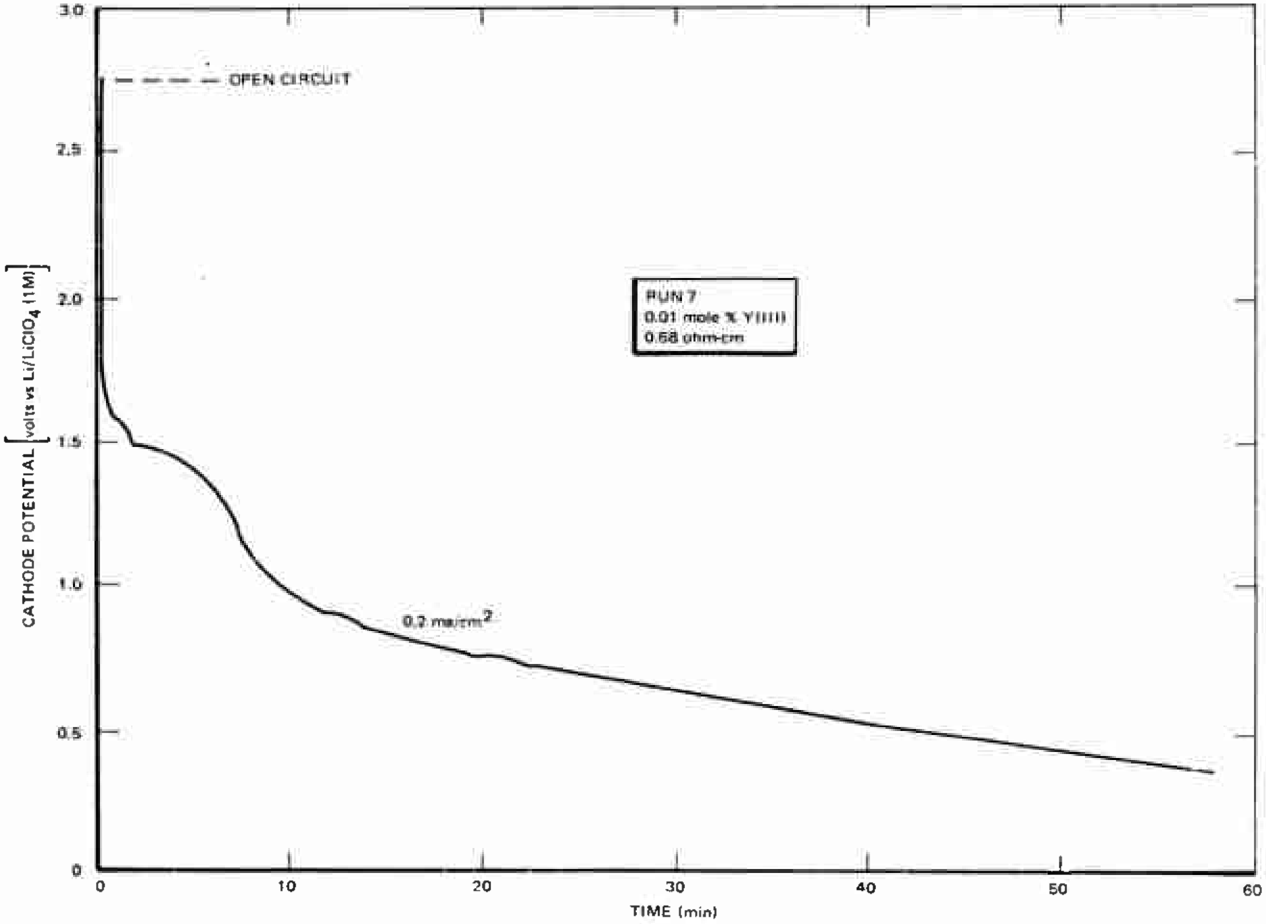

Figure 11. First Continuous Discharge of 0.68 ohm-cm Cadmium Fluoride Crystal at 0.2 ma-cm^2

a potential above 2.0 v. Essentially no discharge capacity remained at this stage, however, as illustrated by Figure 12.

Two passivation mechanisms may be readily envisioned--coating of the crystal by an impervious layer of cadmium metal or of lithium fluoride. Further experimental study will be required to distinguish between these, and possibly other, passivation processes. The electrode was reactivated on exposure to water, as indicated by recovery of the discharge capacity. This effect is shown in Figure 13 for a 0.68 ohm-cm crystal. Although some of the discharge capacity increase may have been due to surface roughening, the restoration of cathodic activity was unmistakable. Whether this occurred by the dissolution of lithium fluoride, or by water-induced detachment of the cadmium metal from the underlying crystal, has not yet been determined.

3. Crystal Electrode Response to Anodic Current

The preparation of secondary cathodes by anodizing cadmium metal in complex fluoride-organic solvent electrolytes has been reported by Shaw and McClelland.(2,13) Doped crystals of the type used in the present study will not be reconstituted from the metal by anodic charging. It was of interest, nevertheless, to examine briefly the behavior of a discharged semiconductor electrode under anodic current. The results are shown in Figures 14 and 15.

At a charging current density of 0.2 ma/cm^2, the total cathode potential rose in 13 min to 8.7 v vs Li/LiClO$_4$(1 M). Of this final value, nearly 6 v appeared to be a non-ohmic component associated with the semiconductor/electrolyte interface. This is indicated in Figure 14 by the immediate drop of 5.7 v with interruption of the charging current. The initial voltage step in cathodic discharge at the same current immediately thereafter (Figure 15)

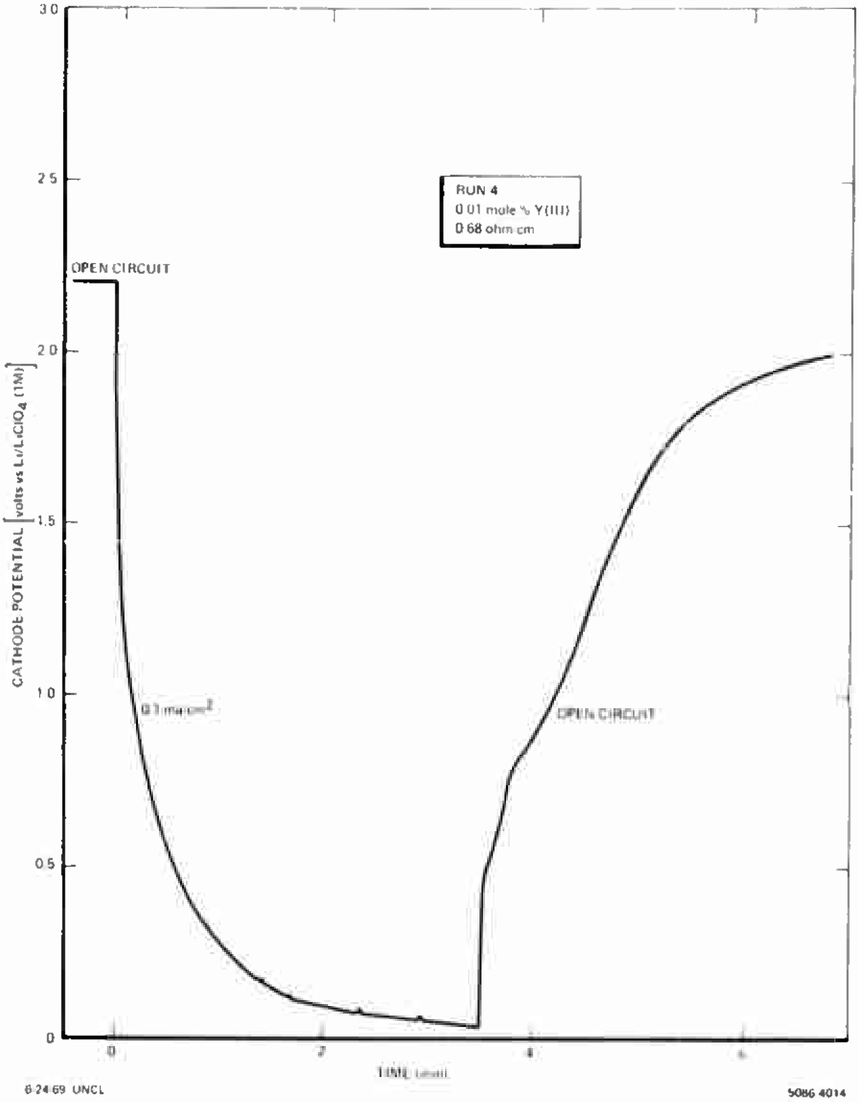

Figure 12. Second Continuous Discharge of Cadmium Fluoride Crystal and Recovery on Open Circuit

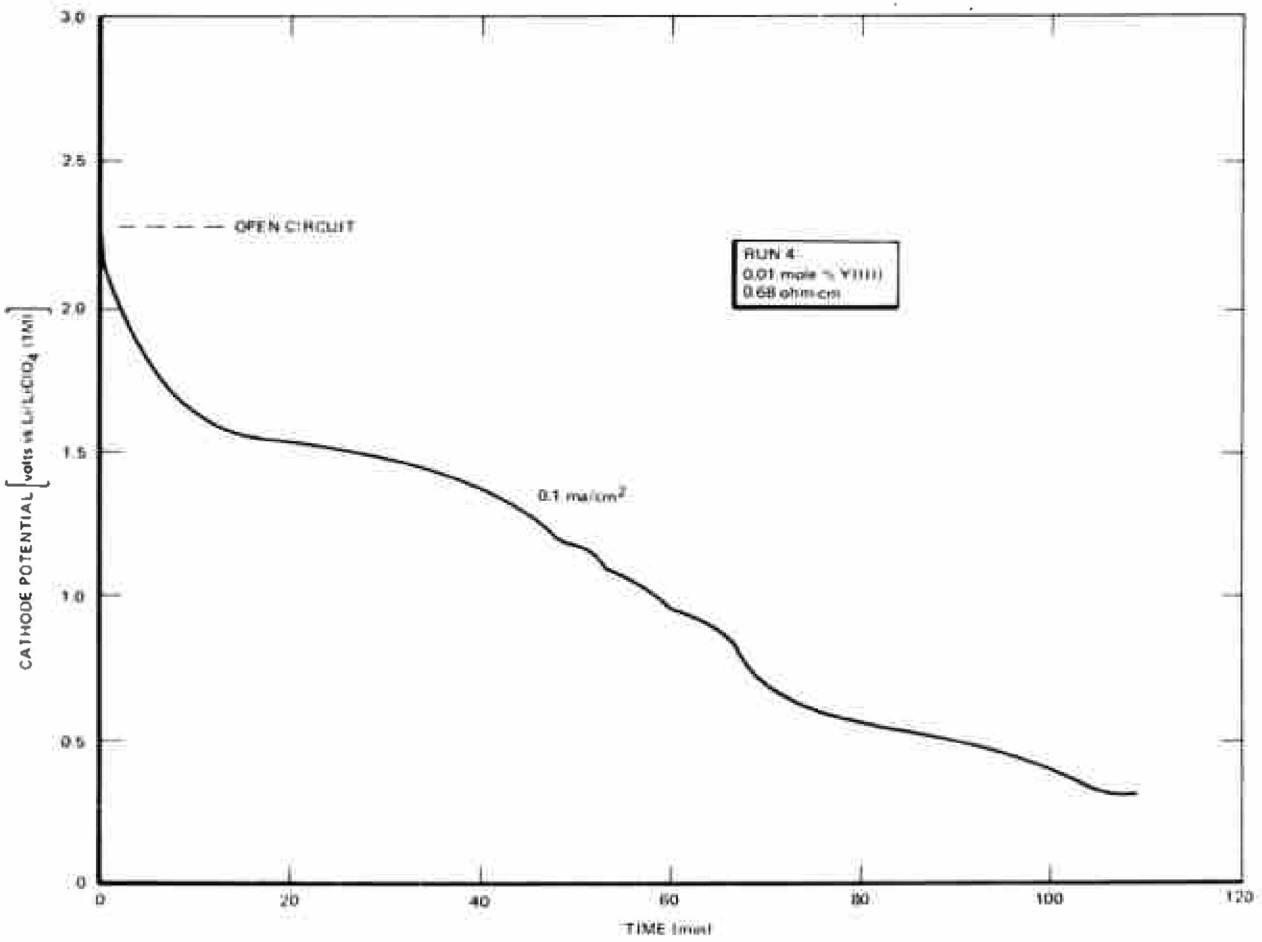

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Figure 13. Effect of Water on Discharged Cadmium Fluoride Crystal

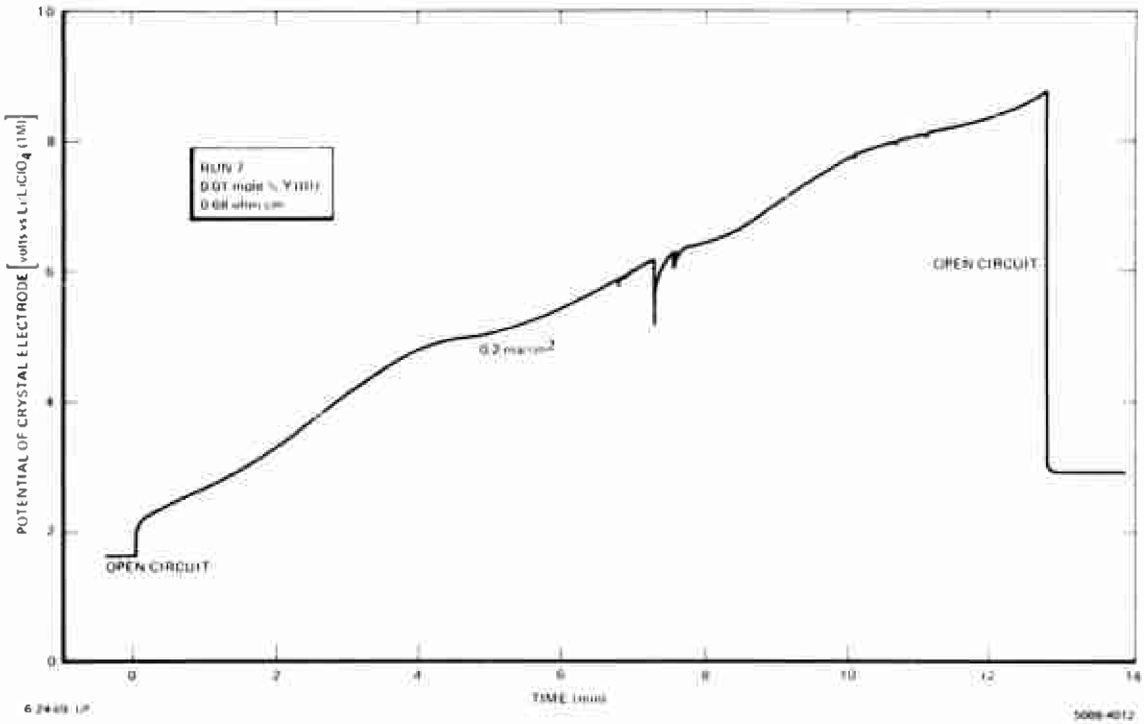

Figure 14. Charging of Previously-Discharged Cadmium Fluoride Crystal

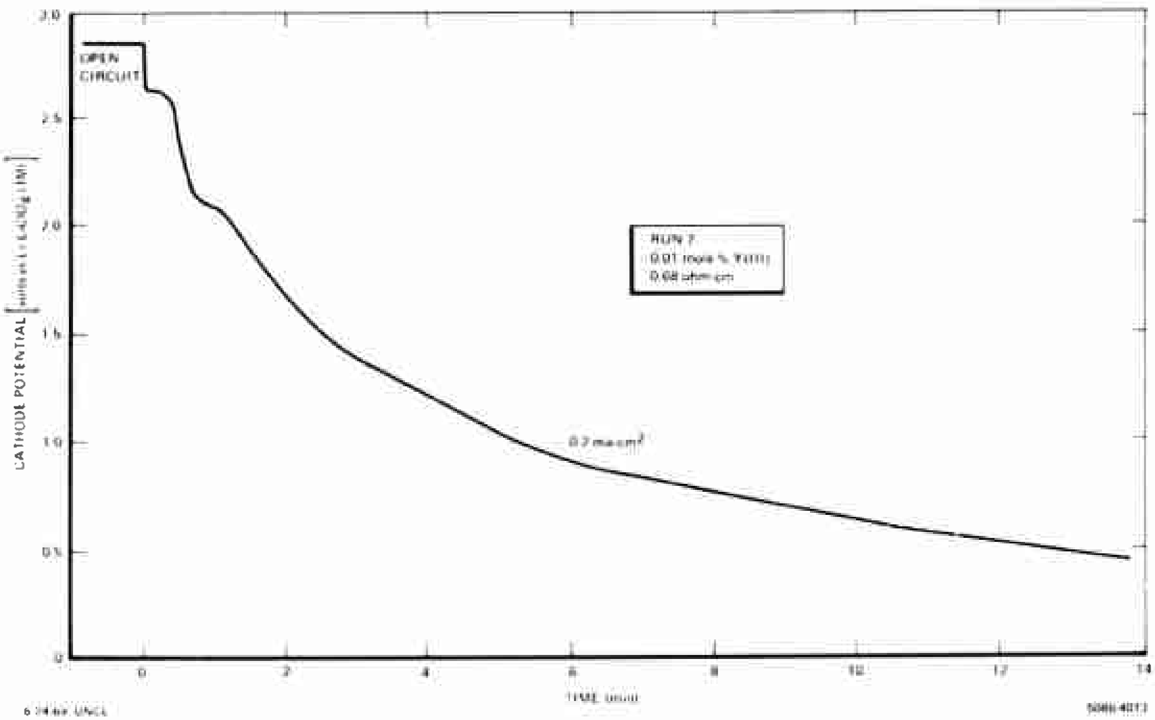

Figure 15. Discharge of Cadmium Fluoride Crystal After Charging to 8.7 v vs Li/LiClO$_4$ (1 M)

was only 0.25 v. This asymmetric behavior is not unexpected for an n-type crystal, at which oxidations should be generally difficult because of the tendency to form an exhaustion layer at positive potentials. In fact, high electric fields have been deliberately created in n-type cadmium fluoride by anodic polarization of the crystal in a tetraethylammonium bromide-acetone solution.(14) The purpose was to study electroluminescence of the rare earth dopant. Other investigators used a similar blocking contact between an electrolyte and n-type cadmium sulfide to study tunneling processes in that system.(15) In the present case, some discharge capacity in the cadmium fluoride potential region did result from charging, but the anodic process occurred with low energy efficiency.

D. IMPLICATIONS FOR PRACTICAL BATTERY CATHODES

Certain observations on the single-crystal electrodes may be used to estimate the performance of porous cathode plates containing n-type cadmium fluoride as the active ingredient. Several correlations are made in the following paragraphs.

The electronic reduction mechanism offers an alternative reaction path for cathodic discharge of cadmium fluoride. In a porous electrode, this route created by doping the solid oxidizer may supplement or supplant another process, such as the reduction of dissolved cadmium ion. To utilize the electronic mechanism, however, one must provide a low-resistance contact at the semiconductor/current collector surface. Adequate contact at a cadmium fluoride/carbon interface is unlikely, but this study shows that a metallic current collector such as indium amalgam should be satisfactory. Good contacts were much easier to produce on crystals containing 1 mole % yttrium than on those with lower dopant concentrations.

The passivation effect described in Section III-C-2 must be overcome or mitigated in the development of practical semiconductor cadmium fluoride electrodes. Modification of the electrolyte by changing the cation or the solvent probably offers the best approach to the solution of this problem. Alternatively, very small crystallites of cadmium fluoride might be used.

In any comparison of discharge characteristics for smooth and porous electrodes, the relative surface areas must be taken into account. Attention must be given to the initial particle size and area loading of the active material as minimum considerations. The effects of plate thickness and porosity, and resistivities of the various phases present, should be included in a more detailed analysis. Figure 16 shows the calculated ratio of current densities ($i_{projected}/i_{actual}$) as a function of particle size for electrodes containing cubic crystallites of cadmium fluoride. The loading of active material is indicated on each line in equivalents/cm^2 and in amp-hr/cm^2. A usable loading of 0.025 amp-hr/cm^2 is typical of a high-performance commercial battery electrode such as silver, while a loading of 0.006 amp-hr/cm^2 is representative of an experimental silver chloride cathode in an organic electrolyte.(16) Uniform current density throughout the thickness of the porous plate was assumed in the construction of Figure 16. With that approximation, the current density of 0.1 ma/cm^2, which was used for discharge of the cadmium fluoride crystals, would correspond to the projected current density of 1.8 ma/cm^2 on a 0.0067 amp-hr/cm^2 porous electrode if the particle size were 10 microns. With a discharge capacity of 0.027 amp-hr/cm^2 and the same particle size, the corresponding projected current density would be 7 ma/cm^2. These comparisons are based on areas only and do not reflect such factors as the decrease of

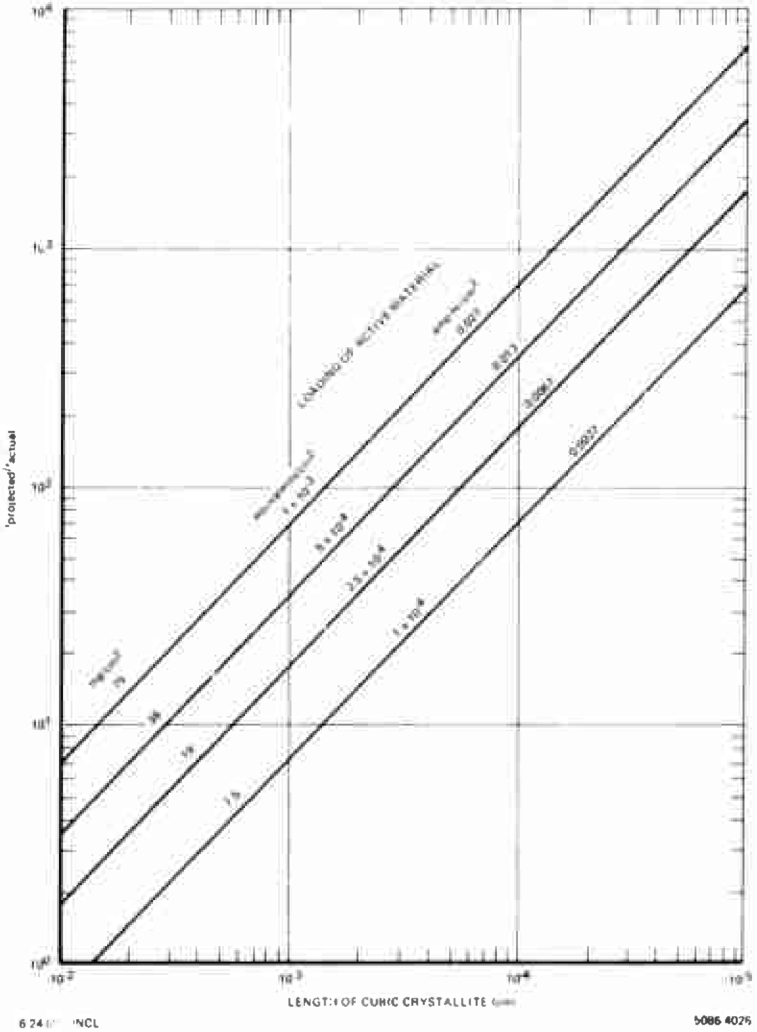

Figure 16. Current Density Ratio for Cadmium Fluoride Electrodes

efficiency with plate thickness, or with passivation of the active surface. If porous cadmium fluoride cathodes can be made to perform as well, on an actual current density basis, as the crystal electrodes performed in this study during the utilization of a 0.1 to 0.2 micron thickness, a practical energy density of 250 whr/lb would be expected, according to Table 5.

V. RECOMMENDATIONS FOR FUTURE WORK

The following studies are recommended for the continuation of this research:

1) Investigation and control of cathodic passivation of cadmium fluoride in organic electrolytes, in order to increase the utilization efficiency

2) Comparative rate study of electronic and other discharge mechanisms for cadmium fluoride, to assess further the improvement in performance that can be achieved by doping

3) Continued efforts to produce and evaluate semiconducting transition metal halides, to provide more active higher-energy cathode materials.

VI. PERSONNEL

Dr. M. M. Nicholson was the principal investigator for this program. Most of the experimental work was performed by Mr. G. L. Shoop. Mr. J. S. Nohl, of the North American Rockwell Science Center, prepared the single crystals and assisted in writing Section III-A of this report.

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VIII. APPENDIX

Table 6 contains detailed data from which the bulk and contact resistivities of six cadmium fluoride crystals were evaluated. The results are summarized in Table 3 and Figures 4 and 5.

TABLE 6

RESISTIVITY DATA FOR YTTRIUM-DOPED CADMIUM FLUORIDE

Crystal Specimen		Current Density[a] (ma/cm^2)	Potential Differences[b] (mv)			Bulk Resistivity (ohm-cm)	Contact Resistances[c] (ohm-cm^2)	
Number	Conditions		H-1	F	G		F	G
5-1	0.01 Mole % Y(III); contacts in place overnight	0	0.3	0.2	-0.2	-		
		0.89	0.3	91	-670	-	102	[illegible]
		-0.89	0.09	-590	120	-	[illegible]	[illegible]
		1.77	0.4	115	-910	-	65	[illegible]
		-1.77	0.1	-765	151	-	450	[illegible]
		3.51	0.9	143	-1190	1.0	41	[illegible]
		-3.51	0	-960	176		270	50
		8.67	2.0	160	-1590	0.9	21	[illegible]
		-8.67	-0.4	-1240	217		165	[illegible]
		17.1	5.2	225	<-1600	1.2	13	-
		-17.1	-0.7	-1530	260		89	[illegible]
5-2	0.01 Mole % Y(III); initial measurements	0	0.1	0.02	0.001	-	-	-
		0.83	0.39	85	-529	~ 2[d]	[illegible]	[illegible]
		-0.82	-0.135	-546	[illegible]	~ 0.6[d]	[illegible]	[illegible]
		1.64	0.65	108	-770	~ 1.6[d]	[illegible]	[illegible]
		-1.62	-0.4	-843	75	~ 1.0[d]	[illegible]	[illegible]
		[illegible]	1.8	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	-0.9	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	2.75	[illegible]	[illegible]	1.4	[illegible]	[illegible]
		-7.63	[illegible]	[illegible]	126	[illegible]	[illegible]	[illegible]
		[illegible]	5.1	194	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	<-1600	[illegible]	[illegible]	[illegible]	[illegible]
	F surface freshly cleaved	[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible] Mole % Y(III) [illegible]	0	[illegible]	[illegible]	[illegible]			
		[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	-	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

See p 46 for footnotes

(Continued)

TABLE 6 (Continued)

Crystal Specimen		Current Density[a] (ma/cm²)	Potential Differences[b] (mv)			Bulk Resistivity (ohm-cm)	Contact Resistance[c] (ohm-cm²)	
Number	Conditions		H-J	F	J		F	J
2-5	0.1 Mole % Y(111)	0.66	0.061	-	-	0.24	-	-
		-0.66	-0.066	-	-	0.25	-	-
		1.32	0.127	-	-	0.24	-	-
		-1.32	-0.129	-	-	0.25	-	-
		2.62	0.259	-	-	0.25	-	-
		12.9	1.23	-	-	0.24	-	-
		-12.9	-1.24	-	-	0.24	-	-
2-4	0.1 Mole % Y(111); initial measurements	0.84	0.216	4.65	-5.24	1.01	5.5	5.9
		-0.84	-0.205	-	-	0.96	-	-
		1.69	0.425	8.95	-6.72	0.99	5.3	6.0
		-1.69	-0.415	-	-	0.97	-	-
		3.37	0.845	16.5	-14.7	0.99	4.9	4.4
		-3.37	-	-	-	-	-	-
		16.7	0.416	54.4	-173	1.02	[illegible]	[illegible]
		-16.7	-0.416	-	-	1.02	-	-
	Recleaned in benzene	0.84	0.309	6.40	-6.86	1.44	7.6	5.2
		-0.84	-0.255	-	-	1.19	-	-
		1.69	0.575	11.4	-14.3	1.34	6.7	5.5
		-1.69	-0.550	-15.0	10.7	1.25	[illegible]	[illegible]
		3.44	1.12	19.1	-32.3	1.49	[illegible]	[illegible]
		-3.44	-1.15	-32.1	16.6	1.32	[illegible]	[illegible]
		16.6	5.52	57.1	-302	1.51	5.4	[illegible]
		-16.6	[illegible]	-288	53.7	[illegible]	17.3	[illegible]
	Recleaned (above); contacts left in place overnight	0.84	0.267	[illegible]	[illegible]	1.54	[illegible]	[illegible]
		-0.84	-0.246	-	-	[illegible]	-	-
		1.69	0.543	[illegible]	[illegible]	1.31	[illegible]	[illegible]
		-1.69	-0.505	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		3.37	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		-3.37	[illegible]	[illegible]	12.0	[illegible]	[illegible]	[illegible]
		16.7	5.44	44.0	-192	[illegible]	[illegible]	[illegible]
		-16.7	[illegible]	[illegible]	42.2	[illegible]	[illegible]	[illegible]
	J surface abraded; cleaned and replaced contacts	16.6	-	[illegible]	-315	-	[illegible]	[illegible]
		-16.6	-	-1400	165	-	[illegible]	[illegible]
	J surface cleaved; replaced J contact	16.6	-	117	[illegible]	-	[illegible]	[illegible]
		-16.6	-	[illegible]	[illegible]	-	[illegible]	[illegible]
6-1	1 Mole % Y(111)	0	[illegible]	[illegible]	[illegible]	-	-	-
		[illegible]	[illegible]	142	[illegible]	-	[illegible]	[illegible]
		[illegible]	-1.4	-1020	[illegible]	-	[illegible]	[illegible]
		[illegible]	0.075	157	<-1000	-	[illegible]	-
		-1.72	-1.2	[illegible]	[illegible]	-	[illegible]	[illegible]
		[illegible]		[illegible]	-	-	[illegible]	[illegible]
		-3.44	[illegible]	[illegible]	[illegible]	-	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]	-	-	[illegible]	-
		[illegible]	[illegible]	[illegible]	[illegible]	-	-	[illegible]
		[illegible]	-0.57	[illegible]	-	-	[illegible]	-
		[illegible]	[illegible]	-	[illegible]	[illegible]	-	[illegible]

See p 46 for footnotes

(Continued)

TABLE 6 (Continued)

Crystal Specimen		Current Density[a] (ma/cm²)	Potential Differences[b] (mv)			Bulk Resistivity (ohm-cm)	Contact Resistances[c] (ohm-cm²)	
Number	Conditions		H-1	F	G		F	G
[illegible] (Cont'd)	Recleaned in benzene; replaced contacts; let stand overnight		[illegible]	[illegible]	[illegible]	-	-	-
		[illegible]	.115	14[illegible]	-1[illegible][e]	[illegible]	28	[illegible][e]
		-[illegible]	-[illegible]	-[illegible]	113	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]67	[illegible]	<-[illegible]	0.49	[illegible]	-
		-1.7[illegible]	-0.1[illegible]	[illegible]	[illegible]	0.41	[illegible]	[illegible]
		[illegible]	0.[illegible]	44[illegible]	-	0.4[illegible]	[illegible]	-
		-[illegible]	-0.[illegible]	-94	[illegible]	0.4[illegible]	77	[illegible]
		7.64	[illegible]	[illegible]	-	0.4[illegible]	76	-
		-[illegible]	-[illegible]	-1[illegible]	[illegible]	0.45	-	[illegible]
		14.[illegible]	1.[illegible]05	730	-	[illegible]	[illegible]	-
		-15.5	-1.770	-	510	0.45	-	55
		[illegible]	[illegible].556	970	-	0.44	42	-
		-27.7	-[illegible].105	-	[illegible]	0.44	-	[illegible]
	As above; G surface freshly cleaved	0	0.[illegible]	[illegible]	0.[illegible]	-	-	-
		[illegible].50	0.12[illegible]	142	-0.40	0.5[illegible]	160	[illegible]
		-0.5[illegible]	-0.07[illegible]	-[illegible]	0.[illegible]3	-	477	0.4[illegible]
		[illegible].77	[illegible].21[illegible]	[illegible]	-0.[illegible]	0.47	[illegible]	[illegible]
		-1.75	-[illegible]	-7[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
		5.5[illegible]	[illegible]	16[illegible]	-1.[illegible]	0.4[illegible]	[illegible]	[illegible]
		-[illegible]	-0.47[illegible]	-[illegible]	1.[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	1.[illegible]	[illegible]	-[illegible]	[illegible]	[illegible]	[illegible]
		-[illegible]	-0.975	<-[illegible]	[illegible]	[illegible]	-	[illegible]
		17.5	[illegible]	[illegible]	-0.57	0.45	15.[illegible]	[illegible]
		-16.3	-1.87	-	5.[illegible]	0.45	-	[illegible]
		[illegible].7	[illegible]	[illegible]	-[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	-	1[illegible]	[illegible]	-	[illegible]

[a] With a negative current, electrons flow from contact F into the semiconductor.

[b] [illegible], [illegible], [illegible] and [illegible] are identified in Figure 1; the F and G potentials were measured with respect to the nearest probe.

[c] [illegible] indium amalgam contacts.

[d] Omitted from average reported in Table [illegible].

[e] Magnitude decreasing with time.

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13 ABSTRACT

The improvement of cathode performance in primary organic electrolyte batteries by conversion of the active material to an electronic semiconductor was investigated in this program. A series of n-type cadmium fluoride single crystals was prepared by a two-stage high-temperature doping process. Initial efforts to prepare n-type manganous fluoride by analogous procedures did not yield a conductive material. The cadmium fluoride crystals were characterized by the measurement of bulk and contact resistivities, using indium amalgam contacts. The crystal specimens were then examined electrochemically by cathodic discharge at constant current density in a lithium perchlorate - propylene carbonate electrolyte.

An electronic mechanism for the discharge of n-type cadmium fluoride was confirmed by the observation of cadmium deposition at the semiconductor/electrolyte interface. An undoped crystal was inactive when examined in the same electrode configuration. Two problems were encountered in the use of semiconducting cadmium fluoride as a cathode material: (1) passivation of the crystal surface, and (2) a requirement for careful preparation of the contact between the semiconductor and the external circuit. Recommendations for future work include investigation of the passivation process and means for its control, comparison of reaction rates for electronic and other discharge mechanisms, and continued efforts to prepare semiconducting transition metal halides.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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