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AD-B000 985

NEW CATHODE MATERIAL FOR HIGH ENERGY-DENSITY BATTERIES

M. M. Nicholson

Rockwell International Corporation
Canoga Park, California

July 1974

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NEW CATHODE MATERIAL FOR HIGH ENERGY-DENSITY BATTERIES

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AD NO.
DDC FILE COPY

[redacted]

[redacted]

31 Jul[redacted]74 [redacted]

Final Report [redacted] 1 Oct[redacted]73—30 Jun[redacted]74

[redacted]

[redacted]

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
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[redacted]

Unclassified

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY *(Corporate author)*

Atomics International Division
Rockwell International Corporation
8900 DeSoto Ave., Canoga Park, CA 91304

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP
N/A

3 REPORT TITLE

NEW CATHODE MATERIAL FOR HIGH ENERGY-DENSITY BATTERIES

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Scientific. Final. 1 October 1973 to 30 June 1974

5 AUTHOR(S) *(First name, middle initial, last name)*
Margie M. Nicholson

6 REPORT DATE
31 July 1974

7a. TOTAL NO. OF PAGES
49

7b. NO. OF REFS
31

8a. CONTRACT OR GRANT NO.
F19628-74-C-0068 new

b. PROJECT NO.
8659-04-01

c. 61102F

d. 681308

9a. ORIGINATOR'S REPORT NUMBER(S)
AI-74-61 ✓

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
AFCRL-TR-74-0386

10 DISTRIBUTION STATEMENT
Distribution limited to U.S. Government agencies only; Proprietary Information; 19 September 1974. Other requests for this document must be referred to AFCRL/PHF, Hanscom AFB, Massachusetts 01731

11 SUPPLEMENTARY NOTES
Tech, Other

12. SPONSORING MILITARY ACTIVITY
Air Force Cambridge Research Laboratories (PH)
Hanscom AFB, Massachusetts 01731
Contract Monitor: Richard Payne/PHF

13 ABSTRACT

The investigation of semiconductor cathode materials for organic-electrolyte batteries was continued, with emphasis on the development of higher-rate porous plates containing n-type cadmium fluoride as the active ingredient. The problem of maintaining electronic contact through a porous semiconductor of high energy gap was examined in some detail from a fundamental viewpoint, and a systematic approach to the selection of current-collector additives was devised.

Experimentally, the discharge characteristics of miniature porous CdF_2 cathodes in 0.1 M TMA·PF_6-PC were compared with those of a single-crystal electrode which served, on a weight basis, as a high-performance standard. The additive materials were indium-tin solder, graphite, cadmium, sputtered aluminum, and four compounds capable of existing as n-type semiconductors: ZnS, ZnSe, CdSe, and In_2O_3. The best cathode formulation contained CdF_2, In-Sn, In_2O_3, and a polystyrene binder. With a discharge potential of 1.1 v vs Li/Li$^{(+)}$ and a utilization efficiency of 38% in ≈ 11 hr, the performance of this electrode was comparable to that of more advanced plate structures containing semiconductive Ni_3S_2.

approx

403 924

DD FORM 1 NOV 65 1473

Unclassified

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Batteries						
Organic Electrolytes						
Cathode Systems						
Semiconductors						
Electronic Contacts						
Cadmium Fluoride						
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I. INTRODUCTION

Previous research at Atomics International has shown that the conversion of cadmium fluoride to an n-type semiconductor increases its cathodic discharge rate in organic battery electrolytes.(1-5) By studies on single-crystal cathodes, it was confirmed that the enhanced reactivity of the n-type material was due to a discharge mechanism involving the electronic charge carriers. Moreover, when such a reaction path is available, the cathode reactant need not have any appreciable solubility in the electrolyte. Self discharge of the sort encountered with cupric fluoride cathodes is thereby avoided, and a long battery shelf life is expected. Cadmium fluoride was of interest, not only as a model compound in the metal fluoride series, but as a practical battery cathode material, since it offers a theoretical energy density of 399 whr/lb when paired with a lithium anode. Results of related, but less extensive, work on zinc fluoride and manganous fluoride were reported previously.(3-5)

Two problems were encountered in developing porous electrode plates from n-type cadmium fluoride: a) The semiconductor was cathodically passivated in the presence of lithium ions, which would normally exist in lithium battery electrolytes, and b) electronic contact to the semiconductor was difficult to maintain in a porous structure. It was found that passivation could be prevented by using a lithium-free electrolyte, tetramethylammonium hexafluorophosphate in propylene carbonate.(4)* The electronic contact in porous cathodes was the main subject of the present investigation. Fundamental aspects of this problem are discussed in Section II, and an experimental study involving eight different contact materials is reported in Sections III and IV. It will be seen that a semiconductor such as indium oxide may be a more effective contact material for cadmium fluoride than conventional carbon or metal additives. With some further work on plate structures, the cadmium fluoride cathode should be competitive with the semiconductive nickel sulfide system.

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*A good separator would therefore be needed to use this cathode system in conjunction with a lithium anode.

II. ELECTRONIC CONTACTS IN A POROUS CATHODE

Conductive additives for battery cathodes are usually chosen on an empirical basis. Porous carbon has long been used in aqueous "dry" cells and, following this custom, many experimental studies on cathode materials for organic-electrolyte batteries have been done with carbon black or graphite additives. Organic-electrolyte cells containing insoluble semiconductive cathode reactants are limited, typically, to projected cathode current densities of 1 to 2 ma/cm^2.(6,7) An exception is the Ni_3S_2 cathode with a porous aluminum additive, which provides current densities up to 6 ma/cm^2.(8) Such comparisons must be made with caution, however, since the area current density is dependent on the loading of active material, as well as other factors. In the case of Ni_3S_2, a typical loading was 55 ma-hr/cm^2. The current density of 6 ma/cm^2 then corresponded to a theoretical discharge time of 14 hr.

The possibility of achieving higher practical discharge rates with semiconductor cathodes through the use of improved electronic contacts is examined here. Specific emphasis is on n-type cadmium fluoride, which was investigated in this program, but the principles discussed should be applicable to other semiconductive materials in both nonaqueous and aqueous batteries. In the case of cadmium fluoride, single crystals of the n-type material can be discharged to a depth of 6.8×10^{-3} cm in 39 hr at a current density of 0.4 ma/cm^2.(5) If this rate could be maintained on the individual particles within a porous structure, a substantial improvement over existing systems would be possible, since the true surface area for the discharge reaction can be one or two orders of magnitude greater than the projected area of the cathode, and the particle size can be smaller than 6.8×10^{-3} cm.

A. CONTACT REQUIREMENTS

In a simple model, a porous cathode may be visualized as an assemblage of cubic crystallites of side length ℓ, connected into a continuous electrical network through a current collector matrix consisting of an electronic conductor. As an approximation, it will be assumed that the electrochemical reaction occurs on five sides of the cube which are exposed to the electrolyte, while the sixth side is occupied by the electronic contact. This situation is depicted in Figure 1.

Area $5\ell^2$ exposed to electrolyte

Area ℓ^2 occupied by contact

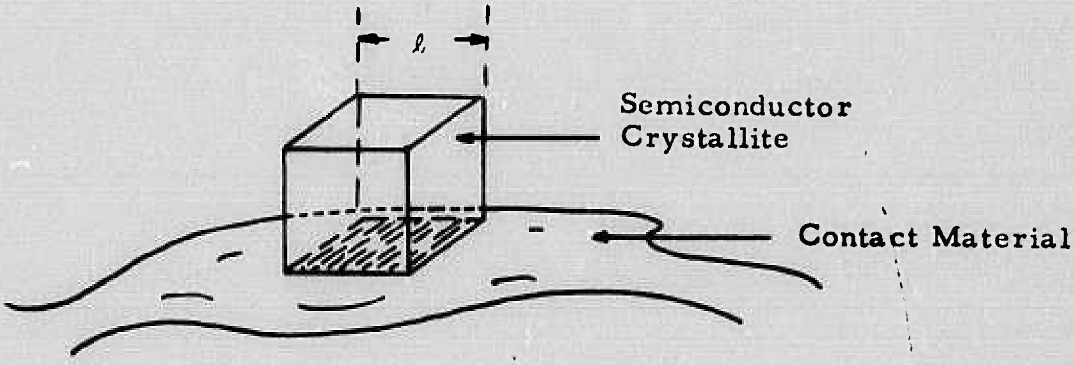

Figure 1. Crystallite with Electronic Contact

With this model, a faradaic current density of 0.4 ma/cm^2, which is attainable on a cadmium fluoride crystal,$^{(5)}$ will require a contact current density of 2 ma/cm^2. Previous consideration of a very similar model showed that a porous cathode with a loading 75 mg/cm^2 of CdF_2 (theoretical capacity 27 ma-hr/cm^2) and a crystallite length of 10^{-3} cm would have a projected current density of 65 times the actual current density on a crystallite face if all six sides of the cube were in contact with the solution.$^{(2)}$ If only five sides were faradaically active, the area factor would be reduced from 65 to 54, and an actual faradaic current density of 0.4 ma/cm^2 would correspond to a projected valued of 22 ma/cm^2, or the C/1.2 rate. Such a performance would be quite good for a lithium cell. An approximate discharge depth from the initial surface of the crystallite to the center can be expressed as $\ell/2$, or 5×10^{-4} cm in the example taken. This distance is less than 1/10 of the depth that is actually dischargeable perpendicular to a single-crystal face in a $TMA \cdot PF_6$-PC electrolyte.$^{(5)}$ Thus, the conditions assumed herein for the model include an adequate precaution against passivation of the cadmium fluoride surface by the metallic layer formed in the discharge reaction.*

To obtain the required contact current density of 2 ma/cm^2, it is assumed that the current collector must make good physical contact with 1/6 of the crystallite surface. The chemical composition of the current collector may also be important, even though it does not undergo a chemical change in discharge of the battery, because the contact material must not form a high potential barrier at the interface with cadmium fluoride. In the present model, the contact should behave essentially as a low ohmic resistance at current densities up to 2 ma/cm^2. If a 0.1-v potential drop is acceptable at this interface, for example, the area resistivity should not exceed 50 ohm-cm^2. This is not a stringent requirement for a low-resistivity semiconductor. On a 0.44-ohm-cm CdF_2 crystal, an area resistivity as low as 0.36 ohm-cm^2 can be obtained with a 50% In-Hg contact.$^{(2)}$ However, since the liquid amalgam does not retain adequate contacts for porous electrodes immersed in an electrolyte, other low-barrier conductors must be considered. Information leading to the selection of candidate materials for this purpose is developed in the ensuing discussion, where it is shown that a number of metals, as well as some semi-conductive additives, may be suitable.

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*As noted in the introduction, the passivation, or eventual blockage of the surface by a reaction product, is much less severe in $TMA \cdot PF_6$ than in a lithium salt.

B. CONTACTS ON WIDE ENERGY-GAP SEMICONDUCTORS

Cadmium fluoride has an energy gap of 6.0 ev.(9) In this respect, it differs markedly from the oxides and sulfides of copper and the transition metals, some of which are useful as battery cathode materials in the presence of conventional additives such as carbon or the parent metal. The latter cathode materials have energy gaps in the vicinity of 2 to 3 ev. Although such cathodes might be improved by more careful selection of the contact materials, the choice is probably less critical than for cadmium fluoride.

Aven and Swank have given several guidelines for the formation of ohmic contacts on wide band-gap semiconductors.(10) The basic approaches are a) to form a low (or negative) barrier at the metal-semiconductor interface or b) to form a very thin barrier through which tunneling can occur. In addition, it should be noted that problems can arise from insufficient solubility of a dopant, thermal or chemical instability of the semiconductor, low-temperature noise generation,(10) and contamination of the interface by adsorbed substances.(11) The use of this information in the preparation of good contacts is discussed below.

1. Low Barriers

Metals with low work functions, i.e., the more active metals, are used as contacts on n-type semiconductors, while metals with high work functions are used on p-type.

Occasionally, a second semiconductor can serve as an intermediate contact between a metal and the semiconductor of primary interest. Successful examples involving n-type semiconductors include In_2O_3 contacts on high-resistivity ZnS,(12) CdO on CdS,(13) and In_2O_3-SnO_2 on CdS.(13)

The barrier between two semiconductors can sometimes be made more diffuse, and hence less troublesome, by forming an interfacial region of nonstoichiometric composition. Aven and Swank suggest the use of a $Zn_xCd_{1-x}S$ layer on n-type ZnS, where x varies from zero to unity, with the metal contact being made between indium and essentially pure CdS.(10)

2. Thin Barriers

A heavily-doped semiconductor with a high carrier density (10^{20} to 10^{21} carriers/cm^3) is more easily contacted than one with low carrier density. It is also advantageous to use a contact material containing a dopant that will provide additional carriers in the region immediately below the interface. Such contacts are usually applied in molten form so that alloy regrowth will occur as the system cools.

3. Clean Interfaces

Films of organic compounds and other insulating materials can introduce additional barriers in the contact region. A good discussion of dirty contacts is given by Harmon and Higier, who note that liquid alloy contacts and those applied by painting or soft pressing are particularly susceptible to this problem.(11) Such contamination is a very probable source of difficulty in battery cathode systems that are formulated with carbon black, organic binders or solvents, or even with inorganic electrolytes which are not exhaustively purified. The best remedy would appear to be the formation of well-bonded contacts throughout the cathode structure before it is exposed to the electrolyte or other sources of contaminants.

4. Contacts for Cadmium Fluoride

Some guidance for the construction of porous cadmium fluoride cathodes may be taken from the foregoing discussion:

a) The work function match should be given careful consideration in the selection of a current collector, since the band gap of CdF_2 is unusually large. This point is developed further in Sections II-C and II-D.

b) The resistivity of n-type CdF_2 containing 0.1 to 1 mole % Y(III) is ~0.4 ohm-cm, and a carrier density of 4×10^{18} electrons/cm^3 has been determined at 0.1 mole % Y(III).(14) It was noted above that 10^{20} carriers/cm^3 will provide a thin barrier in a representative case. Further doping of the CdF_2 might effect some improvement of the contact, but this may not be practical, since the crystals tend to crack at yttrium contents greater than 1 mole %.

c) An effort should be made to form and retain clean, adherent contacts between the metal and the semiconductor which cannot be penetrated by the electrolyte.

C. METAL-SEMICONDUCTOR BARRIERS

Energy barriers on metal-semiconductor surfaces are discussed, for example, by Mead(15) and Swank, (16) with reference to a number of experimental systems. Figure 2(a) is an energy level diagram for an ohmic, or "barrierless" contact on an n-type semiconductor surface at zero current density. Figure 2(b) represents a nonohmic, or rectifying, contact, at which an obstructive barrier exists. The energy differences that are useful in understanding such systems include the band gap E_g, the work function ϕ_s, and the electron affinity χ_s, which is a surface property.* These quantities are defined for the semiconductor in accordance with the energy diagram of Figure 3. The height of the barrier ϕ_b on open circuit is sometimes taken as the difference $\phi_m - \phi_s$ in the work functions of the metal and the semiconductor. The quantity ϕ_s is often given for the flat-band condition and referred to the bulk Fermi level, however. For contact purposes, a better value of the barrier height is considered to be the difference $\phi_m - \chi_s$, which takes into account the bending of the energy bands near the semiconductor surface. (Aven and Swank point out that the flat-band work function on a strongly n-type material is actually nearly the same as the electron affinity;(10) i. e., the Fermi level lies close to the bottom of the conduction band, and the bending is not very pronounced in this case.)

If the barrier height ϕ_b is known, the net current density I through the metal-semiconductor interface may be calculated from the equation

$$I = I^o \exp(-\phi_b/kT) [\exp(qv/kT) - 1] \tag{1}$$

where v is the voltage applied to overcome the effect of the barrier. The term $I^o \exp(-\phi_b/kT)$ may be regarded as an exchange current, by analogy to the corresponding equation of electrochemical kinetics. The quantity I^o can be approximated by the expression

$$I^o \approx 120\, T^2 m^*/m_e \tag{2}$$

where m^* is the effective mass of the majority carrier in the semiconductor, and m_e is that of the free electron. (15) To estimate the current-voltage

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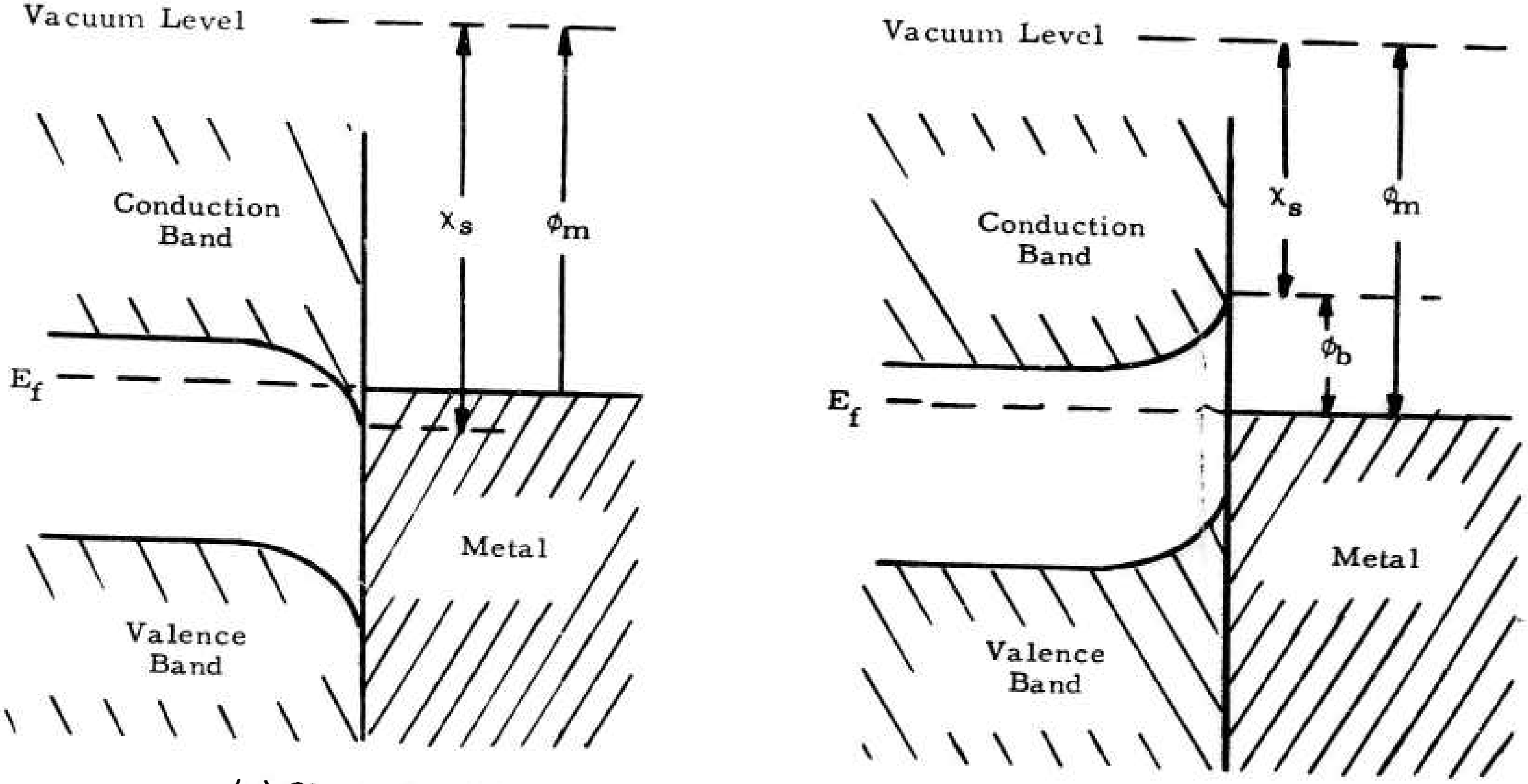
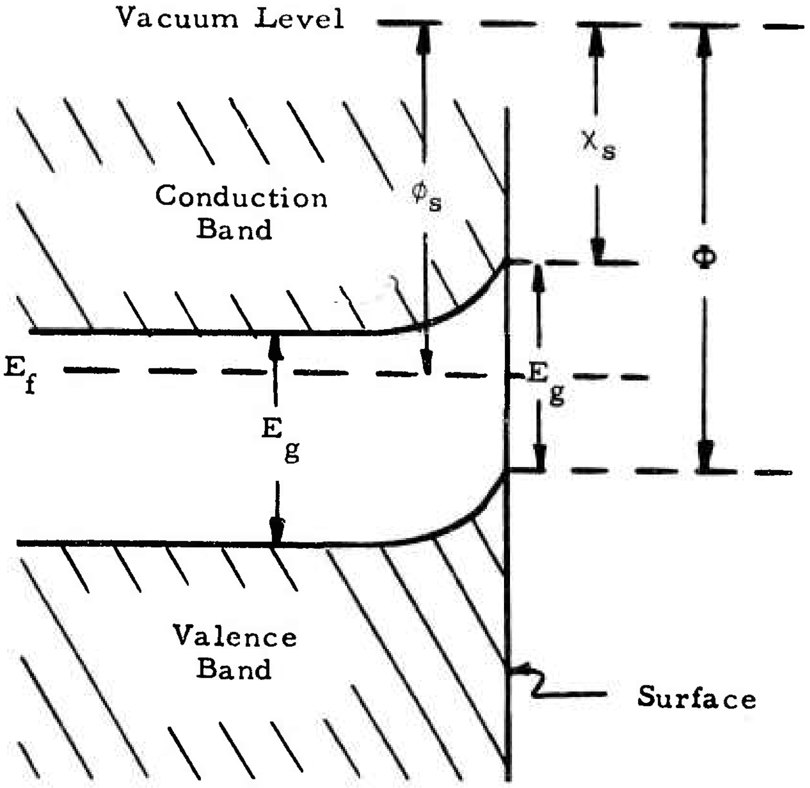
*The subscript s denotes a property of the semiconductor.



(a) Ohmic Contact

(b) Rectifying Contact

Figure 2. Energy Levels at Interface Between Metal and N-Type Semiconductor Under Equilibrium Conditions



<u>Definitions</u>

E_f	Fermi Level in Bulk
E_g	Energy Gap
ϕ_s	Work Function
χ_s	Electron Affinity
Φ	Photoelectric Emission Threshold

Figure 3. Energy Levels at Semiconductor Surface

characteristic for a metal-semiconductor interface, one therefore needs to know the work function ϕ_m of the metal, the work function ϕ_s or electron affinity χ_s of the semiconductor, and the effective mass of the electrons or holes. Some numerical estimates of these quantities for n-type CdF_2 are made in Section II-D.

Although a zero or negative value of ϕ_b is desirable to minimize the voltage drop at the interface and achieve true ohmic behavior, a small to moderate positive barrier may nevertheless be acceptable in a battery electrode. Suppose, for example, that $m^* = 0.4\ m_e$, as for CdF_2,(17) and $I = 2 \times 10^{-3}$ amp/cm^2, as was assumed in discussion of the cubic model. If a voltage loss v of 0.1 v is acceptable under these conditions, Eqs. 1 and 2 indicate that ϕ_b could be as large as 0.65 ev.

D. ESTIMATION OF CONTACT PARAMETERS FOR CdF_2

Apparently no experimental determination has been made of barrier heights for n-type CdF_2 or of ϕ_s or χ_s for this material. It is possible to estimate ϕ_b, however, from correlations involving the energy gaps and Pauling electronegativities(18) which were found by Mead et al. to be valid for a number of semiconductors with medium to large E_g.(15, 19-21) Those investigators determined experimentally that the barrier heights for various metal contacts on zinc and cadmium chalcogenides were linear functions of the electronegativity X_m of the metal. According to Mead, this relationship could be expressed by

$$\phi_b = X_m - X_s \tag{3}$$

where X_s is an "electronegativity" of the semiconductor* found by extrapolating to $\phi_b = 0$. Equation 3 is applicable to ZnO, ZnS, ZnSe, and CdS, all of which have energy gaps greater than 2.4 ev. With contacts on semiconductors of lower E_g, such as CdSe (1.67 ev) and CdTe (1.50 ev), surface energy states due to imperfections of various kinds appear to be more important than the electronegativity of the contact metal in determining the barrier height or the quality of the electronic contact. For the lower-E_g materials, a plot of ϕ_b vs X_m does not have the slope of unity predicted by Eq. 3.

Within the electronegativity-controlled series of semiconductors, Mead has noted that the X_s values for compounds with a common anion differ by an amount equal to the difference in the energy gaps. For example,

---

*The quantity X_s in Eq. 3 is also sometimes called the electron affinity, but this will not be done here, since the X_s and χ_s scales are not referred to the same zero level.

$X_{CdS} - X_{ZnS} = 1.44 - 0.3 = 1.1$ ev and $E_{g(ZnS)} - E_{g(CdS)} = 3.6 - 2.47 = 1.1$ ev. The relationship of X_s to E_g is more complicated with pairs of compounds having a common cation. However, Mead's data for ZnO, ZnS, and ZnSe can be correlated if both E_g and X_a, the electronegativity of the anion, are considered. This is shown in Figure 4, where $X_a - X_s$ is plotted as a function of E_g. The values of X_a are from Pauling's table, and X_s is from the experimental results of Mead et al. The known point for CdS in Figure 4 lies 0.5 ev below the line for the zinc compounds. Although more data would be desirable, a value of X_s can be estimated for CdF_2 by assuming that the zinc and cadmium compounds fall on parallel straight lines, and noting that $X_F = 4.0$ on the Pauling scale. The result is an estimated value of 0.8 for X_{CdF_2}.

Energy barriers for metal-CdF_2 interfaces might now be calculated in accordance with Eq. 3 from the known electronegativities of the various metals. In the case of indium, $X_m = 1.7$, and ϕ_b would be 0.9 ev, which is a fairly large barrier height. However, several investigators have found that indium makes good contacts on n-type CdF_2, as noted in Table 1. Hence, the barrier height from Eq. 3 may be too high in this case. It should be recognized that the figure of 0.8 for X_{CdF_2} is an approximation which may be in error by several tenths of a unit. Nevertheless, Eq. 3 could be useful in comparing the behavior of different metal contacts.

It is also of interest, as suggested in Part C of this section, to re-examine the barrier height estimate obtained from Eq. 4:

$$\phi_b = \phi_m - \chi_s \tag{4}$$

To do so, an estimate of χ_s must be made for CdF_2. This can be done as follows: Swank has given experimental work functions (ϕ_s) and electron affinities (χ_s) for the zinc and cadmium chalcogenides obtained from photoemission, contact potential, and surface photovoltage measurements.(16) These are experimental values, not based on the Pauling approach. A summary and comparison of results from Swank's and Mead's investigations is given in Table 2. In particular, it is seen that Mead's X_s value is approximately 3.4 ev below Swank's χ_s for the four compounds where this comparison can be made. Adding this amount to X_{CdF_2} gives a value of 4.2 ev for χ_{CdF_2} on Swank's scale.*

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*In making this estimate, one assumes that the correlation of χ_s values in Figure 4 is applicable to CdF_2, even though the barrier height based on $X_m - X_{CdF_2}$ may be somewhat high.

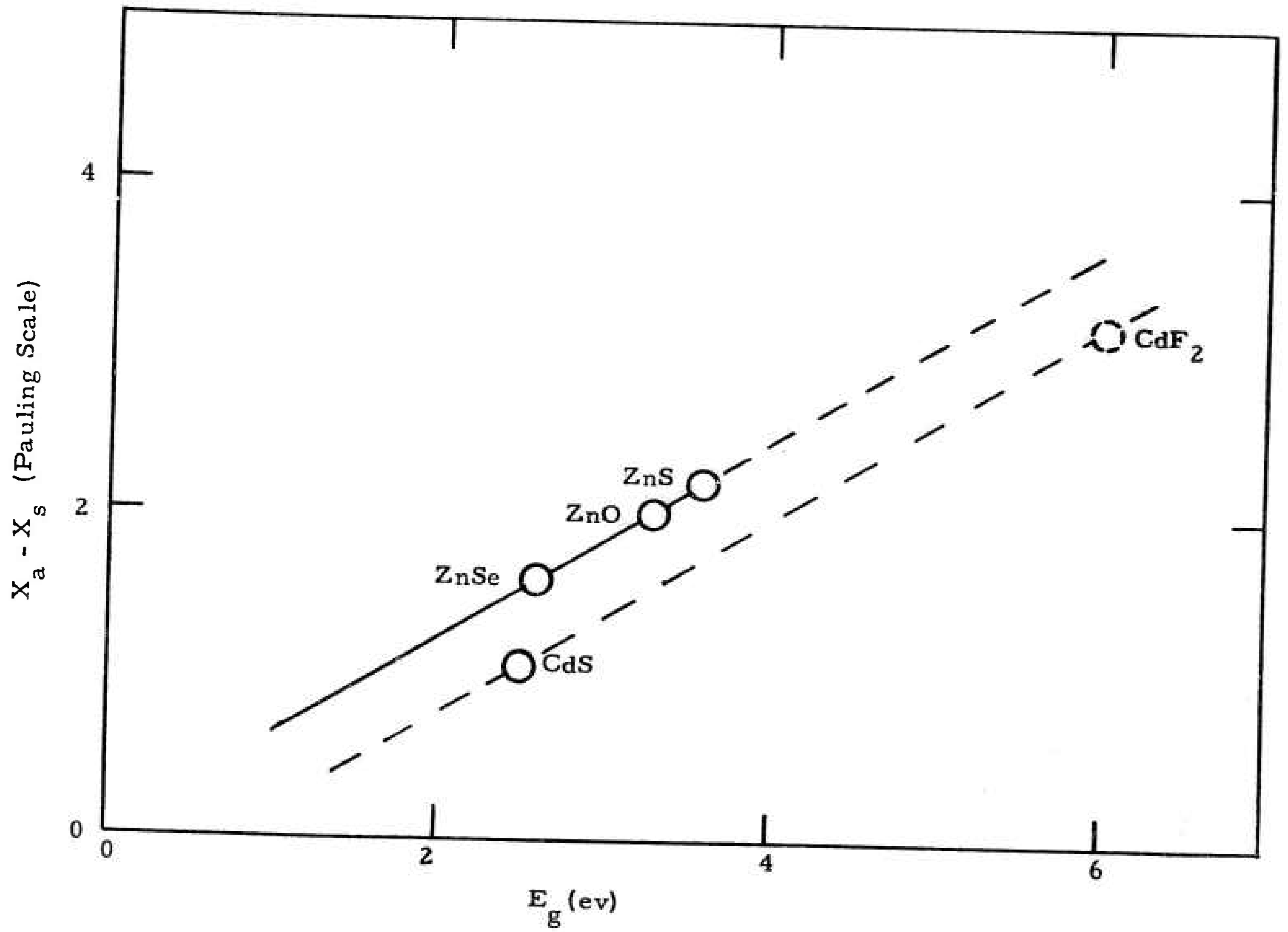

Figure 4. Graphical Estimation of the Electronegativity of CdF_2

TABLE 1

ELECTRONIC CONTACTS ON N-TYPE CADMIUM FLUORIDE[a]

Contact Material	Method of Application	Contact Characteristics	Reference
In	Indium-soldered	Ohmic near 25°C Poor near -196°C	Weller(14)
In	Not described	Ohmic at 25 to -78°C	Lambe et al.(22)
In	Sputtering	Ohmic	Skorobogatov et al.(23)
In-Hg	CdF_2 cleaned in con. HCl; wetted with amalgam; wires attached with In solder.	Satisfactory for measurement of Hall coefficients	Prener and Woodbury(17
In-Hg (50%)	Freshly cleaved CdF_2 contacted with amalgam[b]	Ohmic near 25°C	This investigation(2, 5)
In-Ga	Alloy paste	Ohmic	Skorobogatov et al.(23)
Au	Sputtering	Nonohmic[c]	Skorobogatov et al.(23)

[a] Single-crystal CdF_2

[b] Wetting improved by exposure to air

[c] Desired for electroluminescence study

TABLE 2

SEMICONDUCTOR PROPERTIES RELATED TO CONTACT QUALITY[a]

Semi-conductor	E_g Energy Gap(16)	ϕ_s Work Function(16)	X_s Electron Affinity(16)	X_s Electro-negativity	$X_s + 3.4$	$\phi_{In} - X_s$	Indium Contact Quality(16)
ZnO	3.25	4.68	4.57	1.5(19)	4.9	-0.49	Ohmic
ZnS	3.6	5.4	3.9	0.3(20)	3.7	0.2	Sometimes Ohmic
ZnSe	2.73	4.84	4.09	0.8(19)	4.1	-0.01	Ohmic
ZnTe	2.23	5.43	3.53	--	--	0.55	Nonohmic
CdS	2.47	5.01	4.79	1.4(20)	4.8	-0.71	Ohmic
CdSe	1.67	5.22	4.95	--	--	-0.87	Ohmic
CdTe	1.50	4.67	4.28	--	--	-0.20	Ohmic
CdF_2	6.0(9)	--	~4.2	0.8[b]	4.2	~-0.1	Ohmic[c]

[a] Energies are in electron volts; X is on Pauling scale.

[b] Estimated from Figure 4

[c] Table 1

It is now possible to calculate barrier heights for CdF_2 from Eq. 4. Work functions of a number of metals are listed, for convenience, in Table 3. Figure 5 shows that this approach may indeed provide a useful criterion of contact quality, with negative "barriers" corresponding to good contacts and positive barriers to poor ones. The indium barrier on CdF_2 is found in this way to be -0.1 ev. The contact should be ohmic, and this is consistent with experience. Moreover, the indium barriers on the chalcogenides fall into the same pattern. These are given as $\phi_m - \chi_s$ in Table 2. Ohmic contacts are difficult to prepare with indium on ZnS, where $\phi_m - \chi_s = 0.2$ ev, and not feasible on ZnTe, where $\phi_m - \chi_s = 0.55$ ev. For the five other chalcogenides in the table, however, the barrier is negative, and ohmic contacts are easily made.

E. CANDIDATE MATERIALS FOR CONTACTS ON N-TYPE CdF_2

Figure 5 indicates that good contact should be attainable on cadmium fluoride with indium, aluminum, cadmium, manganese, magnesium, tin, and possibly titanium and chromium. Uncertainties in specific cases arise from the fact that some work function data for the metals are not in agreement. Values for zinc range from 3.08 to 4.65 ev,$^{(24)}$ and two values were plotted for one metal in several instances. All of the work function points necessarily fall on the line in this figure, since it represents the relationship

$$\phi_b = \phi_m - 4.2 \tag{5}$$

where 4.2 is the estimated value of χ_s for CdF_2. Contacts of graphite and the noble metals do not appear promising. In accordance with this trend, Skorobogatov et al. found that nonohmic contacts were produced by sputtering gold on n-type CdF_2.$^{(23)}$

Other candidates for conductive additives may be found among the zinc and cadmium chalcogenides listed in Table 2. Those with electron affinities (χ_s) below 4.2 ev, which is the estimated value for CdF_2, include ZnS, ZnSe and ZnTe. CdTe (4.28 ev) and ZnO (4.57 ev) may also be considered. To form a conductive porous structure, these materials should be incorporated in finely divided CdF_2, along with an appropriate metal such as indium which (in most cases) makes good contact with the chalcogenide. Experimental results on CdF_2 cathodes with several metal and compound additives are given in Section IV.

TABLE 3

WORK FUNCTIONS OF SOME COMMON METALS

Metal	ϕ_m(ev)		Metal	ϕ_m(ev)	
	Ref. 24	Ref. 25		Ref. 24	Ref. 25
Cs	1.8	--	304 Stainless Steel	--	4.3
Li	2.3	--	Fe	3.9 to 4.8	4.47
Mg	3.7	--	Co	4.4	--
Sn	3.7	--	Ni	5.0	4.41
Mn	3.8	--	Cr	4.6	3.9
Zn	3.0 to 4.6	--	Cu	4.5	4.42
Cd	4.1	--	Hg	4.5	--
Al	4.1	--	C(graphite)	4.6	--
Ti	4.0 to 4.5	3.6 to 4.3	Ag	4.7	--
In	--	4.08	Au	4.8	--
Ga	4.1		Pt	5.3	5.6 to 5.8
Bi	4.2	--			

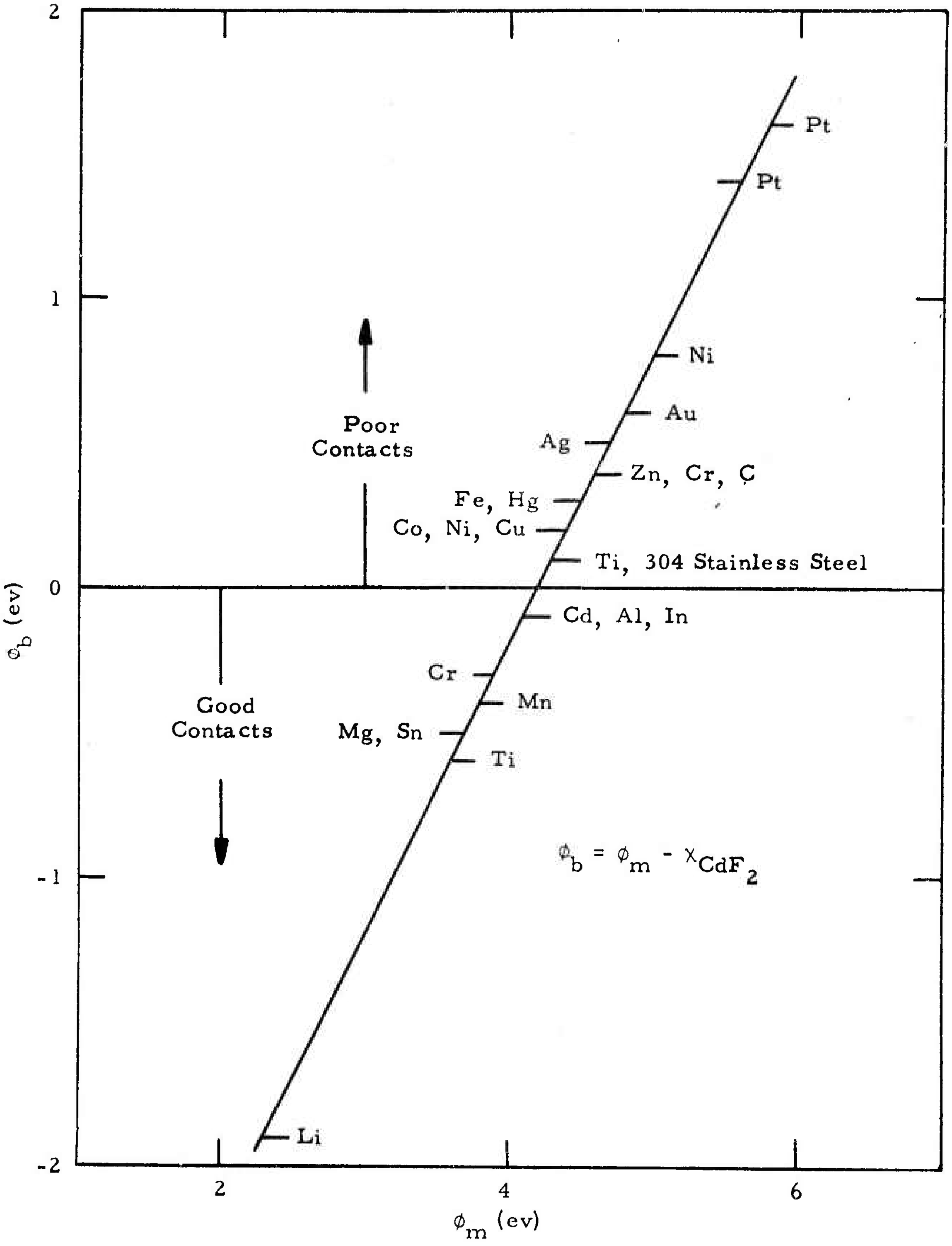

Figure 5. Estimation of Barrier Energies for Contacts on CdF_2

F. SUMMARY OF METHOD FOR SELECTING CONTACT MATERIALS

The principles involved in selection of a cathode current collector may be summarized as follows:

1) For an n-type cathode reactant,* a contact material should be chosen with a work function equal to or lower than the electron affinity of the semiconductor surface.

2) If the electron affinity of the semiconductor is not known, it may be estimated from the energy gap and the Pauling electronegativities of the constituent elements.

3) If necessary, the energy gap of a binary semiconductor may also be estimated by chemical approaches. An excellent review of this subject is given by Vijh.(26)

4) Selection of the contact material is more critical for semiconductors with energy gaps larger than ~ 1.7 ev. Those with smaller gaps tend to form ohmic contacts more easily because of surface energy states which participate in the transfer of electrons across the contact interface.

III. EXPERIMENTAL

Experimental procedures used in the investigation of porous cadmium fluoride electrodes are described in this section.

A. GENERAL PROCEDURES

The preparation methods for n-type cadmium fluoride of ~ 0.4 ohm-cm resistivity,(2) and for the 0.1 M TMA·PF_6-PC† electrolyte(4) have been detailed in other reports. The electrochemical cell(4) and instrumentation(1) were also described previously. Fabrication of the porous cathodes is discussed in Part B of this section.

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*P-Type semiconductors are usually not desirable as cathode materials because their properties are unfavorable for charge transfer at the solution interface.

†Tetramethylammonium hexafluorophosphate in propylene carbonate

The cell was assembled and housed during the electrochemical measurements in an argon-atmosphere glove box at room temperature. All potentials were recorded with reference to an $Li/LiClO_4$ (1 M) electrode in PC, which was connected to the cathode compartment by means of a long salt bridge filled with 0.1 M $TMA \cdot PF_6$-PC. The anode was a lithium plate in $TMA \cdot PF_6$-PC. Two fritted disks separated the anode and cathode compartments to avoid contamination of the cathode by lithium ion.$^{(4)}$ Potential-time curves for 1-min discharges were obtained at current densities ranging from 0.05 to 4 ma/cm^2. Discharge measurements lasting from about 1 to 24 hr were made in most instances at 0.2 or 0.4 ma/cm^2.

B. POROUS ELECTRODE FABRICATION

Descriptions and sources of materials used in the fabrication of porous cathodes are given in Table 4. Powdered n-type cadmium fluoride was prepared as follows: A single crystal of CdF_2 containing 1 mole % Y(III) was cut into slices approximately 1 mm thick. After cleaning, these pieces were sealed into quartz tubes under vacuum and cadmium-fired at 500°C, according to the method of Prener and Kingsley.$^{(27)}$ The fired crystal pieces were subsequently cleaned in 1:1 HCl, dried, ground with a mortar and pestle, and sieved into three fractions with particle sizes of <40, 40 to 230, and >230 μm. This material, which may be designated as "bulk-fired" cadmium fluoride, was used in most of the porous cathodes. It had a resistivity of 0.4 ohm-cm. For a few experiments, a "powder-fired" preparation was made by grinding a doped crystal prior to the high-temperature cadmium exposure. This powder was used without further cleaning; a small amount of cadmium metal therefore remained on its surface from the firing process.

To apply an indium-tin additive, a weighed quantity of the selected powder was stirred with a weighed amount of 50% In - 50% Sn solder, at a temperature slightly above the solder melting point of 116°C. The powder-solder mixture was then cooled to room temperature and mixed with a small amount of <40 μm polystyrene powder. This binder material was prepared by grinding flakes of low-melting Dow PS-2 polystyrene. For electrodes with compound additives, such as In_2O_3, the CdF_2 powder and the additive powder were mixed in the dry state before the solder was applied. The polystyrene binder was later incorporated in the usual way.

TABLE 4

MATERIALS USED IN POROUS CATHODES

Material	Description	Source
CdF_2		
Undoped	Powder, 40 to 230 μm agglomerates, 3N	Research Inorganic Chemical Co.
N-Type	Powder, ground from single crystal, 40 to 230 μm and <40 μm crystallites	This investigation
In-Sn	Solder wire, 50 wt % In, 50 wt % Sn, m.p. 116°C	Electronic Space Products, Inc. (ESPI)
Cd	Splatters, 5N, for Cd-firing of CdF_2	ESPI
Cd	Powder, 200 to 325 mesh, 6N, for cathode additive	ESPI
Graphite, SPEX 1-C	Powder	
ZnS	Powder, high purity	Materials Research Corp. (MRC)
ZnSe	Powder, high purity	MRC
CdSe	Powder, high purity	MRC
In_2O_3	Powder, high purity	MRC
Polystyrene, PS-2	Powder, ground from flakes, <40 μm	Dow Chemical Co.

Pressed cathode plates with the active material confined in a projected area of 0.28 cm^2 were constructed as shown in Figure 6. A silver foil base plate was brushed with molten In-Sn solder and attached, while hot, to a mask of polystyrene foam of the type used for hot beverage containers. The resulting circular cavity was partially filled afterward with a weighed quantity of the selected cathode mixture. The filled electrode assembly was pressed for 3 min between aluminum blocks on a hot plate with a surface temperature of 138°C, under a total applied weight of 5.6 lb. This treatment fused both the In-Sn solder and the polystyrene binder, producing cohesive plates with a final thickness of $\sim$0.5 mm. The electrodes formed in this manner were oriented vertically during the electrochemical measurements. In some cases, the electrical lead to the cathode plate consisted of an expanded nickel strip, rather than a solid strip extending from the silver base plate, as shown in the figure.

The 40 to 230 μm CdF_2 powder was partially coated with sputtered aluminum for one series of experiments.* In this procedure, the powder was spread on a flat dish which travelled slowly around the sputtering chamber. No furthur agitation was applied. The coating process required about 20 min under an argon pressure of several microns and produced a flat-surface aluminum thickness of 0.5 μm. It was estimated that the specimen temperature did not exceed 50°C. Under magnification, good mirror coatings were seen to cover approximately half of the crystallite faces on most of the particles.

Table 5 gives the compositions and theoretical discharge capacities for all of the porous cathodes used in this study.

IV. RESULTS AND DISCUSSION

Cadmium fluoride cathodes containing different types of additives are compared on the basis of 1-min discharge data in Parts A through D of this section. The results of longer discharges are discussed in Part E. Section V provides a summary of conclusions reached in this work and related prior studies on the semiconductor cathode concept.

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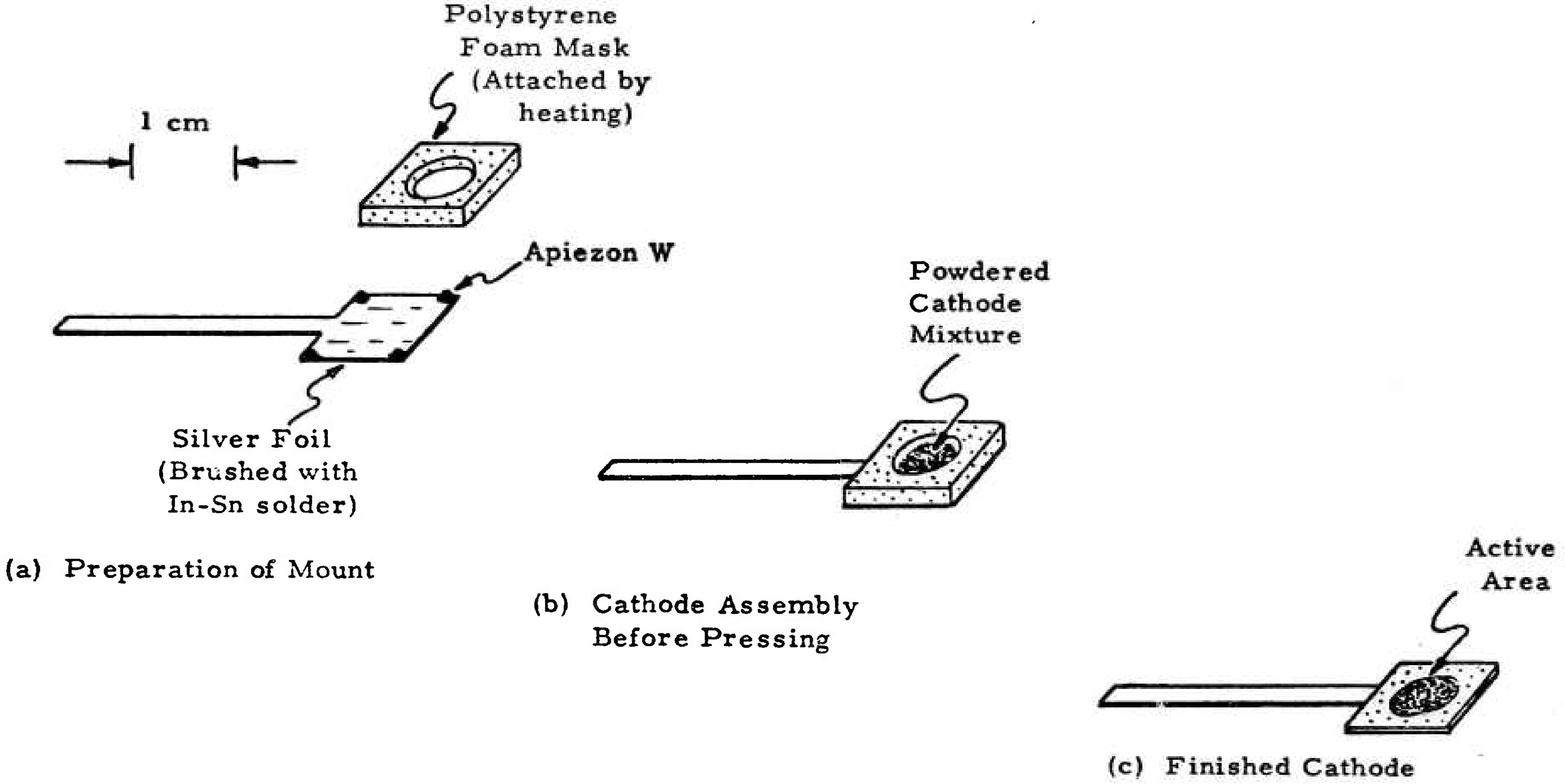
*Sputtering was done by Sloan Technology Corp., Santa Barbara, California



(a) Preparation of Mount

(b) Cathode Assembly Before Pressing

(c) Finished Cathode

Figure 6. Construction of Miniature Porous Cathode Plates

TABLE 5

COMPOSITIONS OF POROUS CATHODES

Cathode	Components (wt %)				CdF_2 Loading (mg/cm^2)	Theoretical Capacity (ma-hr/cm^2)
	CdF_2[a]	In-Sn	PS-2	Other Additives		
1	- (Blank)	(Brushed on silver)	(Mask only)	-	-	-
2	78 (Undoped)	14	8	-	69	25
3	78	15	8	-	84	30
4	69	24	7	-	81	29
5	78 (<40 μm)	13	9	-	78	28
6	78 (<40 μm)	13	9	-	244	88
7	51	49	-	-	276	99

[a] N-Type, ~0.4 ohm-cm, 40 to 230 μm unless indicated

TABLE 5, Continued

Cathode	Components (wt %)				CdF_2 Loading (mg/cm^2)	Theoretical Capacity ($ma\text{-}hr/cm^2$)
	CdF_2	In-Sn	PS-2	Other Additives		
8	91 (Powder-fired)	-	9	-	91	33
9	77	-	7	Cd 16	68	24
10	91	-	9	Al(sputtered)[b]	92	33
11	86	-	5	Al(sputtered) Graphite 9	90	32
12	77	-	8	Al(sputtered)[c] Graphite 15	85	31
13	54	-	3.5	Al(sputtered) Cd 43	103	37

[b] ~0.3% Al in sputtered powder

[c] Refined in Cd vapor

TABLE 5, Continued

Cathode	Components (wt %)				CdF_2 Loading (mg/cm^2)	Theoretical Capacity ($ma\text{-}hr/cm^2$)
	CdF_2	In-Sn	PS-2	Other Additives		
14	34	23	7	ZnS 36	68	24
15	37	21	6	ZnSe 36	68	24
16	35	23	7	CdSe 35	70	25
17	35	22	7	In_2O_3 36	70	25
18	-	22	7	In_2O_3 71	-	-

A. INDIUM-TIN CONTACTS

Short-term discharge data for cathodes containing indium-tin solder as the only conductive additive are shown in Figure 7, where the potentials at the end of 1-min discharge periods are plotted as functions of the current density in ma/g of CdF_2. On an area basis, the Cathode 2 data, for example, cover the range of 0.05 to 8 ma/cm^2. Also included in this figure are polarization curves for a single crystal(5) and a blank electrode mount which had an In-Sn coating brushed on silver. The cadmium fluoride loading in the case of the single crystal was taken as 44 mg/cm^2, which corresponded to the utilization depth of 68 µm that had been observed experimentally at 0.4 ma/cm^2.(5) A fictitious loading of 22 mg/cm^2 was used for the blank electrode, in order to place its current density on an appropriate scale.*

Although none of the In-Sn-type electrodes performed as well as the single crystal, based on Figure 7, all of them were superior to the best porous cathode obtained in the preceding contract period.(5) The latter electrode was a pasted type containing powder-fired CdF_2 without any additives. Its polarization curve is included in Figure 8 of the present report. Pressed Cathodes 3, 4 and 5 represent essentially a 10-fold improvement over the pasted electrode, when compared at the 1.3-v level. To attain the performance of the single crystal, however, a further three-fold increase in current density would be required. It should be noted also that doped Electrodes 3, 4, and 5 were substantially better than the similar undoped one, No. 2, at current densities above 0.7 ma/g CdF_2. The latter current density may be considered a background level.

Cathode 5, prepared from smaller CdF_2 crystallites, was no better than Cathodes 3 and 4, which contained the 40 to 230-µm material. Cathode 6, with a CdF_2 loading of 244 mg/cm^2, was less efficient than Cathode 5, with 78 mg/cm^2. Cathode 7, with a high CdF_2 loading (276 mg/cm^2) and a high solder content (49%), was better than Cathode 6, but not as good as 3, 4, or 5.

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*The blank curve is appropriate for comparisons with Cathodes 2-5 but would be shifted to lower current scales for Nos. 6 and 7, which had heavier loadings of CdF_2.

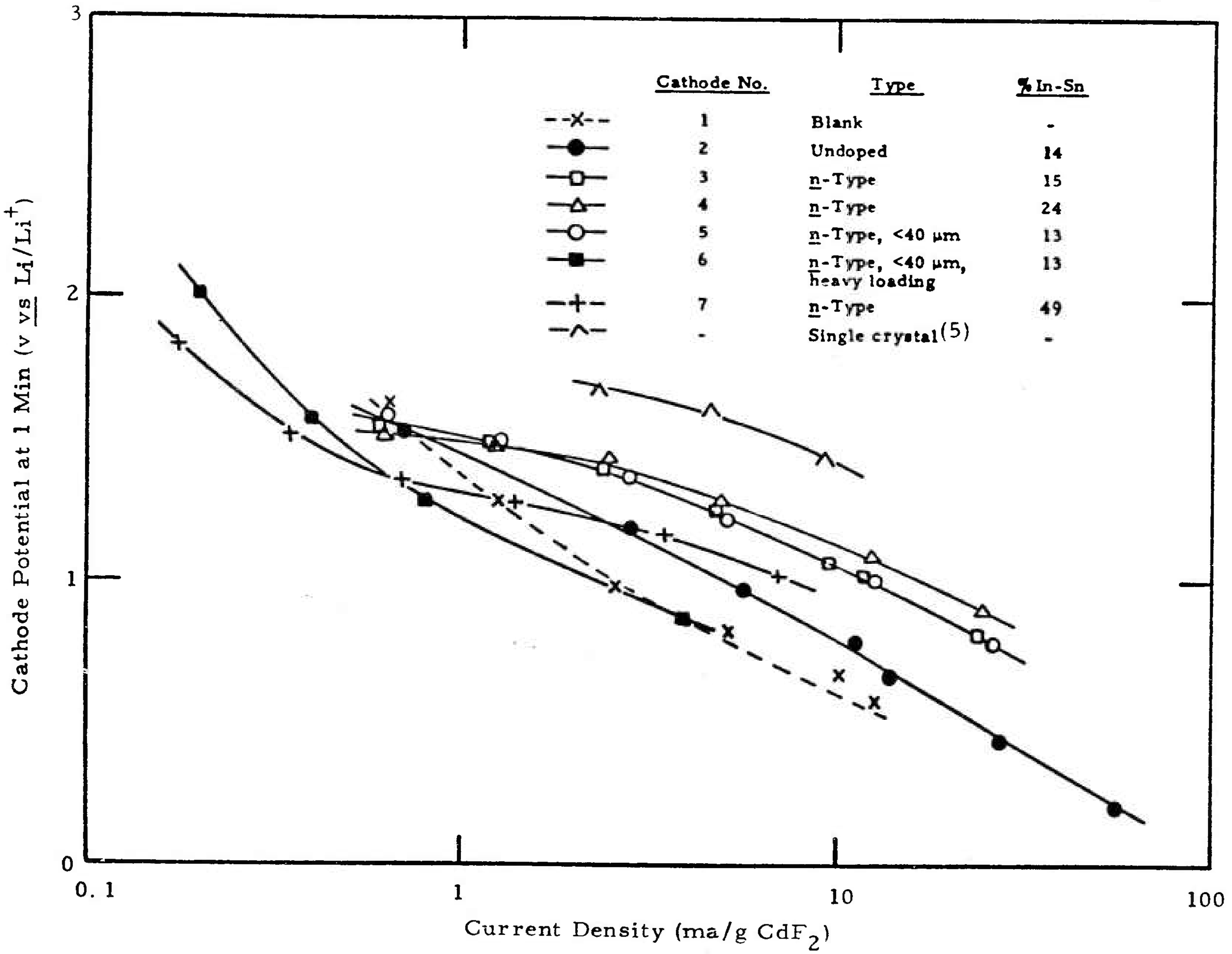


Figure 7. Polarization Curves for CdF_2 Cathodes with Indium-Tin Contacts

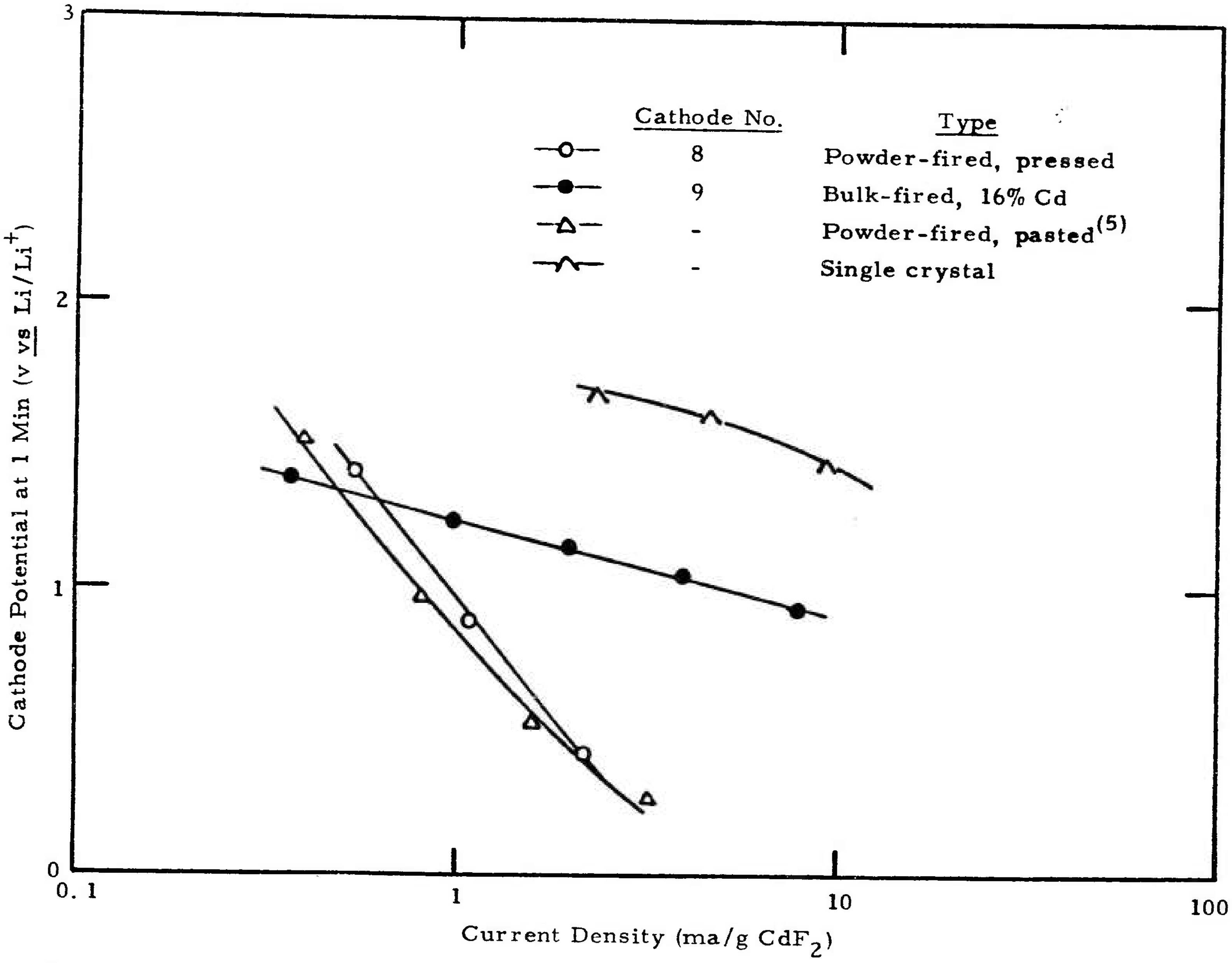


Figure 8. Polarization Curves for CdF_2 Cathodes with Cadmium Contacts

These comparisons indicate that In-Sn is a useful cathode additive but that it probably will not lead to the goal of single-crystal performance in a porous electrode structure when applied by the simple mixing technique described in Section III.

B. CADMIUM CONTACTS

Two types of cadmium contacts were evaluated. The powder-fired material had a thin dark layer of cadmium metal on the surface which was stoichiometrically equivalent to the interstitial fluoride ions produced by doping with 1 mole % YF_3.(27) This layer apparently made a small but significant contribution to the conductive matrix of the electrode.(5) In other cases, the cathode mixtures were prepared with cadmium powder. Results for the cathodes containing cadmium metal are shown in Figure 8. Pressing of the powder-fired material with the polystyrene binder did not appreciably change its discharge behavior. Pressing of bulk-fired CdF_2 with 16% Cd powder produced a much better cathode but one which did not approach single-crystal behavior. Since cadmium metal is very soft, it is likely that the difficulty was in the electrical properties of the CdF_2/Cd interface, rather than the extent of its geometric area. These results suggest that, contrary to Figure 5, cadmium metal may not provide good contacts in the CdF_2 system.

C. SPUTTERED ALUMINUM CONTACTS

In its microscopic appearance, the sputtered aluminum preparation closely resembled the model depicted in Figure 1, with the exception that about half of the facets on each crystallite were covered with the metal. Good interfacial and interparticle contacts should have been present with this kind of microstructure. Nevertheless, the performance of the sputtered material was rather poor, as indicated by Figure 9. Some improvement occurred with the addition of powdered graphite (Cathode 11) or cadmium (Cathode 13). It appeared that the sputtering process might have damaged the semiconductor, possibly through the loss of cadmium metal. Refiring with cadmium produced only minor improvement, however.

D. COMPOUND ADDITIVES

It was noted in Section II that certain semiconductive compounds might produce effective contacts in a porous cathode containing a high energy-gap reactant. In accordance with that suggestion, several compounds were

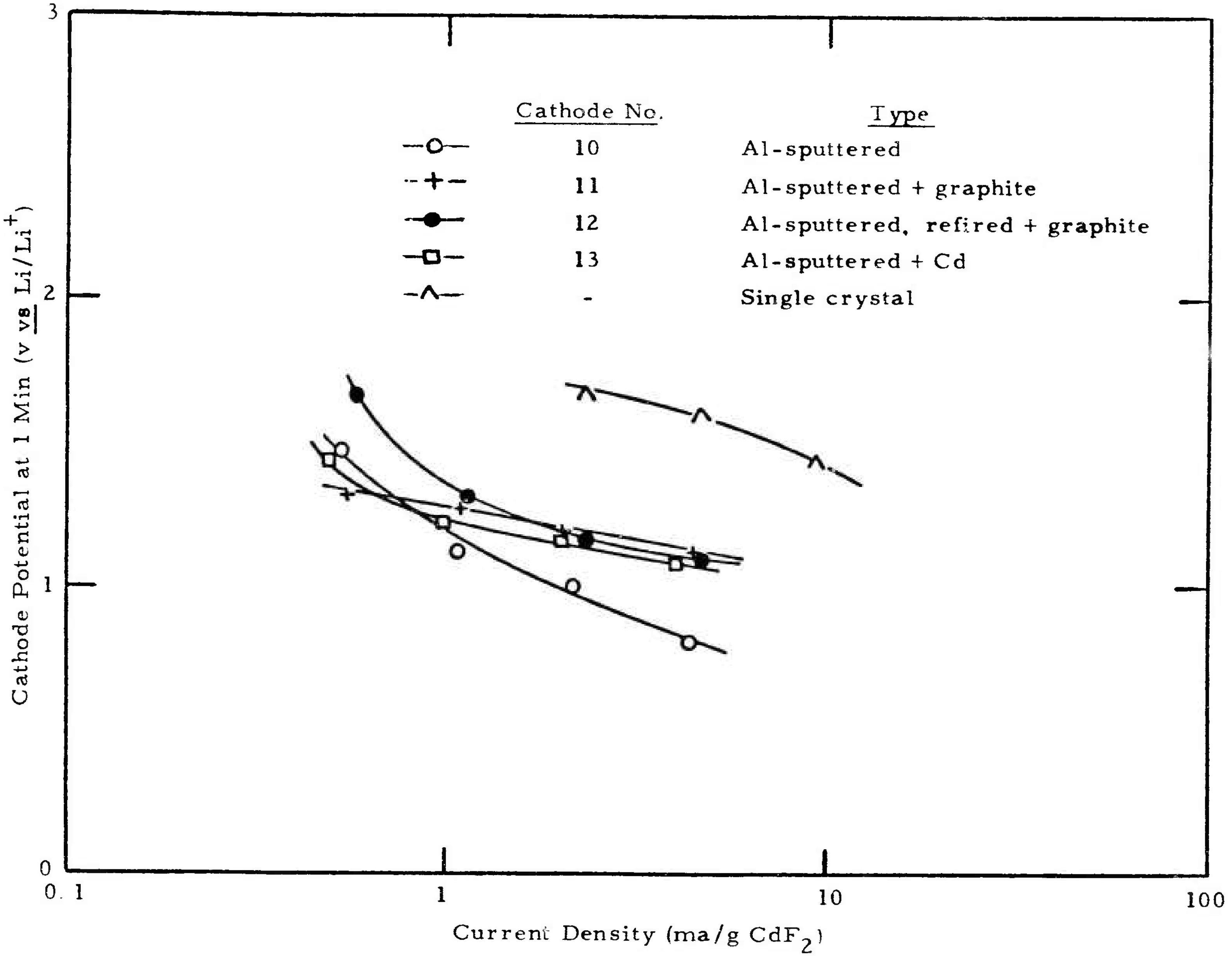


Figure 9. Polarization Curves for CdF$_2$ Cathodes with Sputtered Aluminum Contacts

investigated as additives for the cadmium fluoride cathode. These included ZnS, ZnSe, CdSe, and In_2O_3, all of which are known to form n-type semiconductors when the corresponding metals are present in excess. The additives were used in the form of high-purity powders for these experiments, however, without any specific doping, other than that which may have occurred in contact with the molten In-Sn solder.

Short-term polarization data for cathodes containing cadmium fluoride with the four compound additives are shown in Figure 10. The sulfides and selenides had no pronounced effects; the curves for ZnS, ZnSe, and CdSe are generally similar to those of Figure 7 for the CdF_2-In-Sn formulations. Indium oxide produced an interesting result, however: The polarization curve for Cathode 17 intersected that for single-crystal cadmium fluoride at a current density of 5 ma/g of CdF_2.

In Figure 11, the behavior of the CdF_2-In_2O_3 mixture is compared with that of In_2O_3 alone. The responses at current densities below 8 ma/g of In_2O_3 were quite similar, with and without CdF_2, although the discharge potentials (which ranged as high as 2.6 v vs Li/Li^+) were more consistent with thermodynamic values for the cadmium fluoride electrode. In a cell having the reaction

$$2Li + CdF_2(s) \rightarrow Cd + 2LiF(s),$$

the theoretical potential is 2.70 v, while for

$$6Li + In_2O_3 \rightarrow 2In + 3Li_2O,$$

it is 1.45 v. No significant impurities were found on emission spectrographic analysis of the indium oxide. Further investigation would be required, therefore, to account for the low-current activity that was observed in Figure 11 for In_2O_3 in the absence of CdF_2.

For battery applications, the discharge behavior at higher current densities is of greater importance, and the results in that region were more conclusive. It is apparent from Figure 11 that most of the current above 8 ma/g of In_2O_3 was due to cadmium fluoride. This was verified in longer discharge runs which are discussed in Part E below.

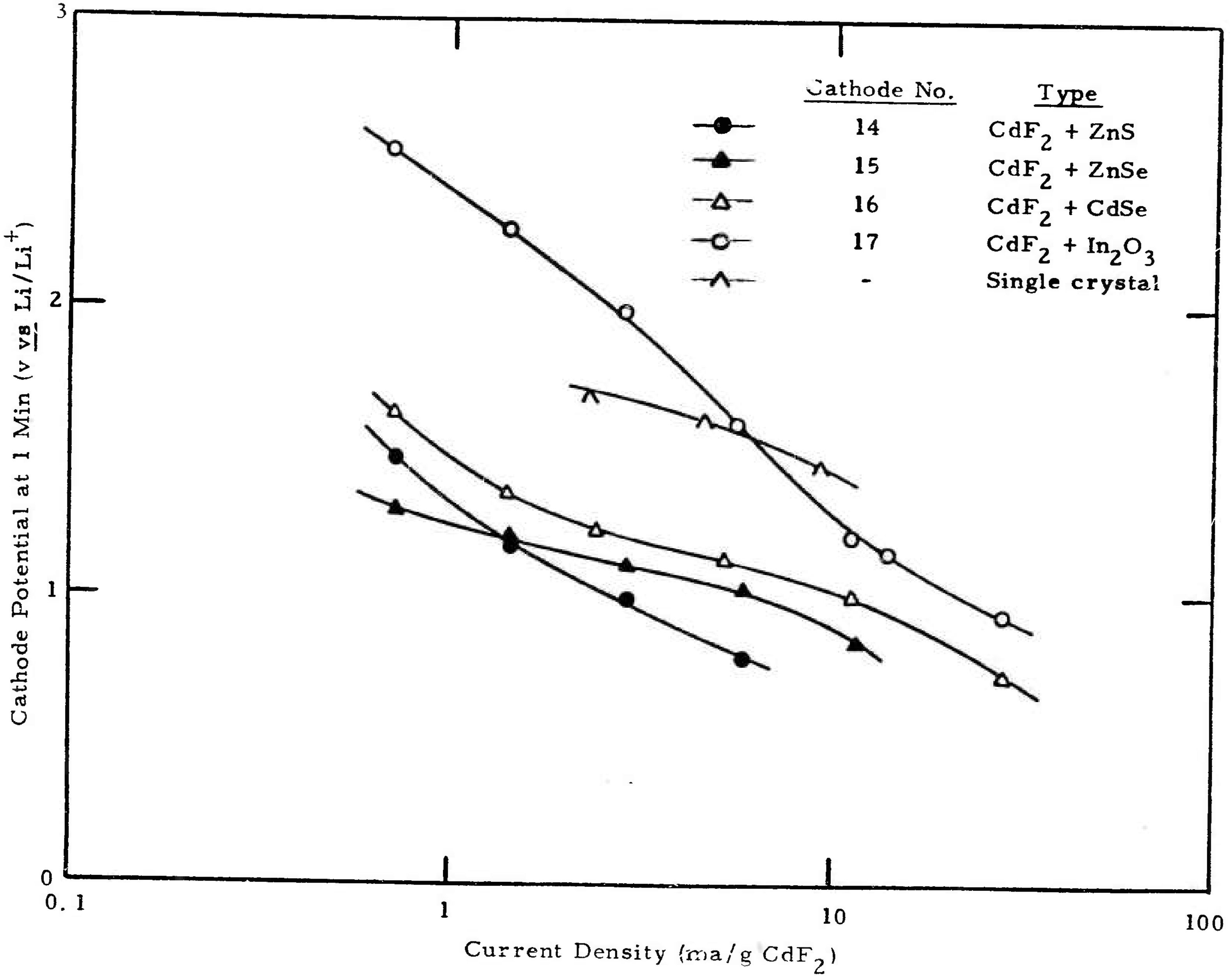


Figure 10. Polarization Curves for CdF_2 Cathodes with Compound Additives

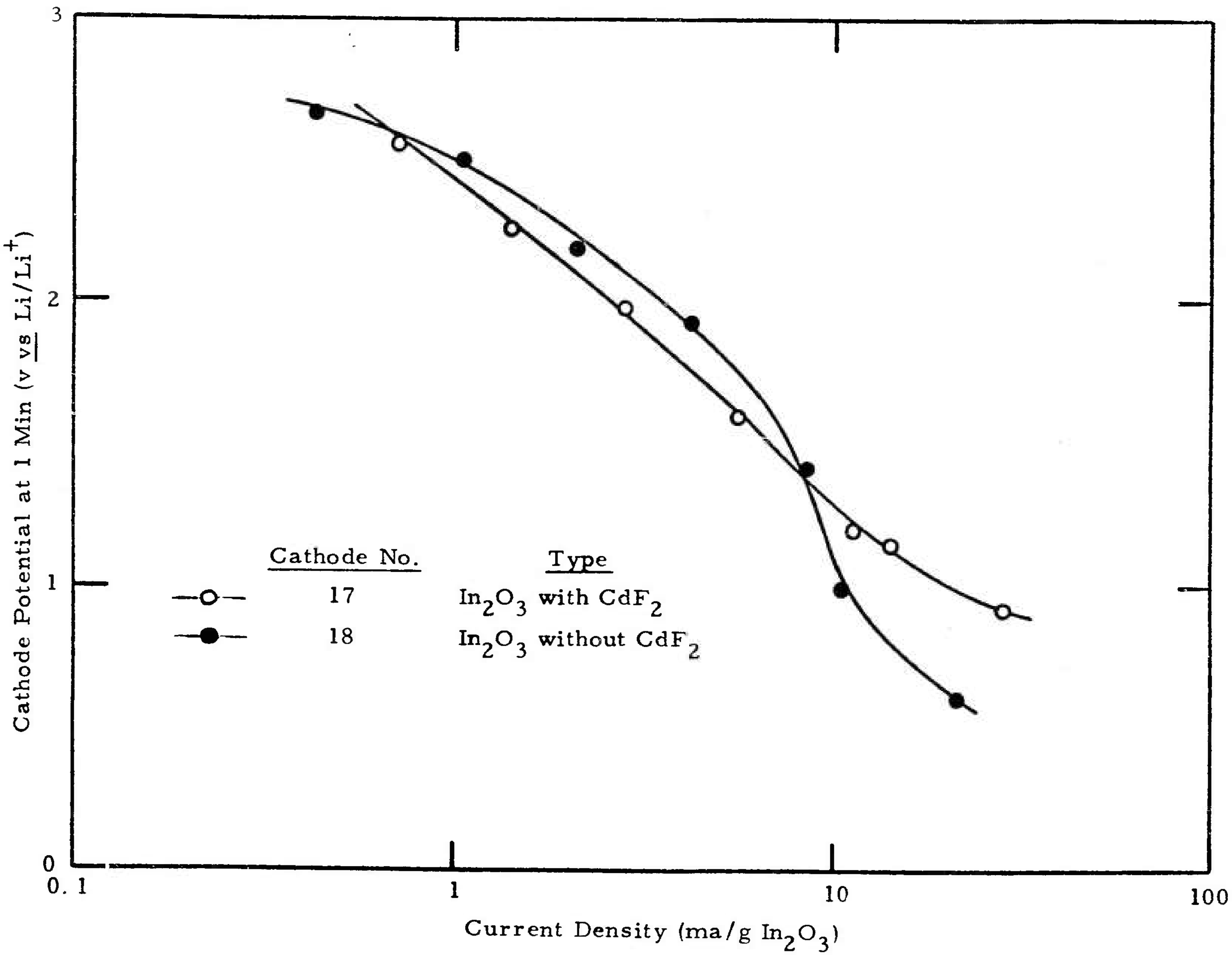


Figure 11. Polarization Curves for In_2O_3 With and Without CdF_2

E. LONG-TERM DISCHARGE BEHAVIOR

Most of the porous cathodes were discharged for 1 hr or more at current densities that were judged to be appropriate on the basis of the 1-min polarization curves. Several of the more promising formulations were further subjected to continuous discharges lasting some 15 to 25 hr. The results of 1-hr discharges for thirteen cathode formulations are summarized in Table 6. These data are generally consistent with the polarization behavior represented by Figures 7-11. Most of the cathodes could support continuous discharge at potentials above 1.0 v for at least 1 hr at current densities of 0.4 to 0.8 ma/cm^2, an exception being Cathode 18, which contained indium oxide without cadmium fluoride.

Figure 12 shows the results of longer discharges for Cathodes 5, 7, 17, and 18, and for a single crystal of <u>n</u>-type CdF_2. Cathode 5, prepared from CdF_2 of particle size <40 μm, underwent a transition at 2 hr to 0.9 v. This final potential is a usual background level following discharge in the TMA·PF_6-PC electrolyte. With a theoretical capacity of 28 ma-hr/cm^2, the utilization of active material in Cathode 5 at the 2-hr transition was only 3%. Cathode 7, with a higher theoretical capacity of 99 ma-hr/cm^2, was dischargeable at 0.8 ma/cm^2 and showed no transition at 25 hr, or 20% of the calculated discharge time. This run was discontinued before completion of the discharge, since the electrode performance was not outstanding on a weight basis.

The best porous electrode examined in this study was No. 17, with the CdF_2-In_2O_3-In-Sn formulation. Thirty-eight percent of the cadmium fluoride was utilized in this case, near 1.15 v, in a discharge run that included 3 hr at 0.4 ma/cm^2, followed by 9.5 hr at 0.9 ma/cm^2. Had all of the discharge occurred at the higher current density, the theoretical life of the cell would have been 28 hr, based on the cadmium fluoride content. The 38% utilization corresponded to a cutoff potential of 0.90 v. Cathode 18, which contained In_2O_3 without CdF_2, discharged near 0.75 v in the first hour. It is probable, therefore, that the reduction of CdF_2 accounted for most of the current in No. 17 to the time of the 0.90-v cutoff. Following this, the smaller plateau region covering a time of about 2 hr may have involved the reduction of In_2O_3 and/or SnO_2.

TABLE 6

DATA FOR CONTINUOUS DISCHARGE OF POROUS CATHODES

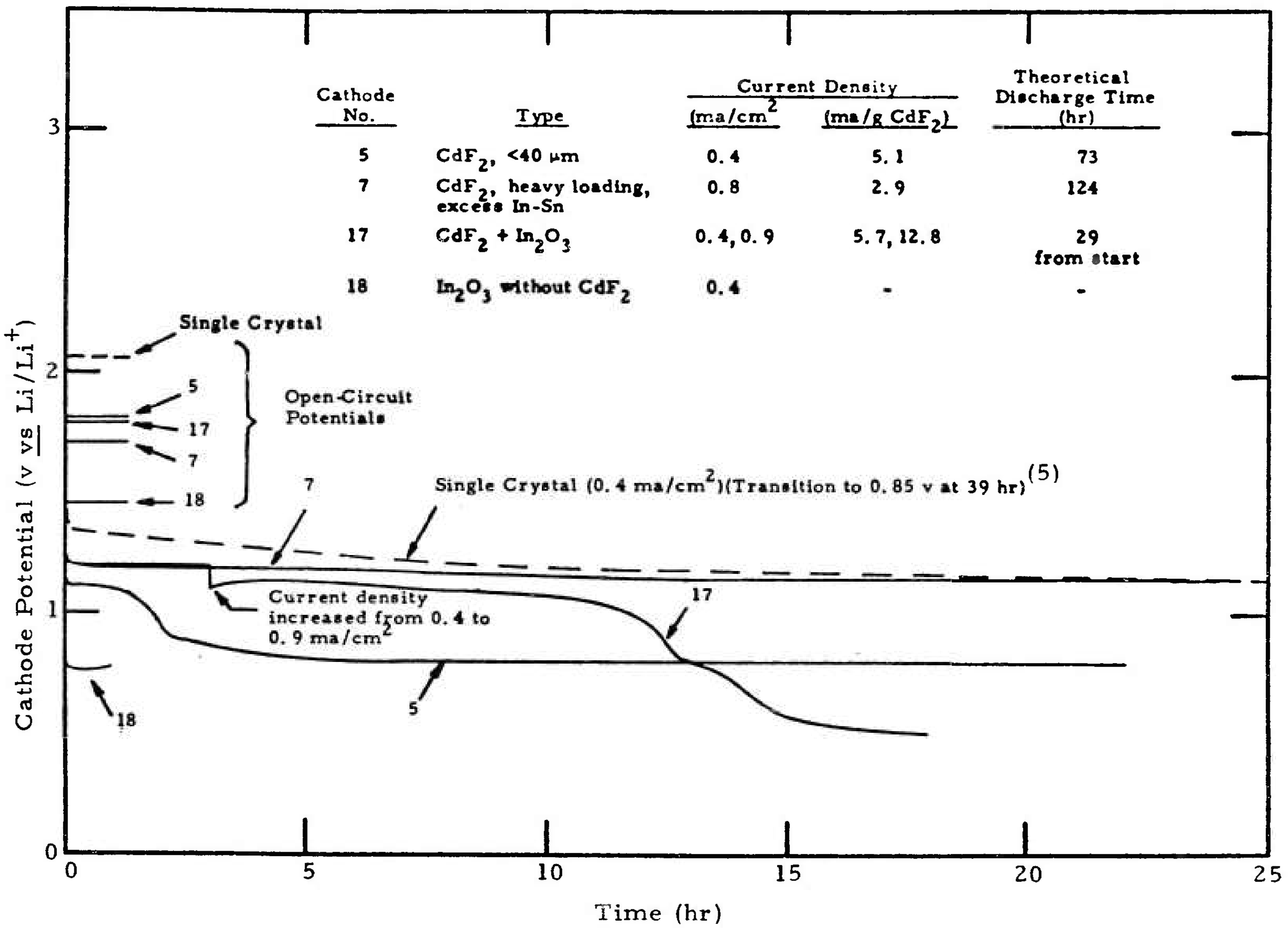
Cathode	Components[a]	Open-Circuit Potentials		Discharge Characteristics		
					Potential	
		Initial (v vs Li/Li^+)	Before Long Discharge[b] (v vs Li/Li^+)	Current Density (ma/cm^2)	0.1 hr (v vs Li/Li^+)	1 hr (v vs Li/Li^+)
2	CdF_2(undoped) In-Sn, PS-2	2.43	2.28	2	0.58	0.52
3	CdF_2 In-Sn, PS-2	2.42	1.95	0.4	1.15	1.15
4	CdF_2 In-Sn, PS-2	2.29	1.76	0.4	1.22	1.22
5	CdF_2(<40 μm) In-Sn, PS-2	2.55	1.82	0.4	1.13	1.10
6	CdF_2(<40 μm) In-Sn, PS-2	2.73	1.57	0.4	1.08	1.05
7	CdF_2 In-Sn, PS-2	2.54	1.71	0.8	1.19	1.19

[a] N-Type CdF_2, 40 to 230 μm, unless indicated.

[b] After several 1-min discharges.

TABLE 6, Continued

Cathode	Components	Open-Circuit Potentials		Discharge Characteristics		
		Initial (v vs Li/Li$^+$)	Before Long Discharge (v vs Li/Li$^+$)	Current Density (ma/cm^2)	Potential	
					0.1 hr (v vs Li/Li$^+$)	1 hr (v vs Li/Li$^+$)
9	CdF_2 Cd	2.76	1.52	0.4	1.08	1.10
10	CdF_2 Al(sputtered) PS-2	2.65	1.59	0.2	1.11	-
11	CdF_2 Al(sputtered) Graphite	2.73	1.73	0.2	1.19	1.21
12	CdF_2 Al(sputtered) Graphite	2.66	1.56	0.2	1.20	1.23
13	CdF_2 Al(sputtered) Cd	2.72	1.62	0.2	1.17	1.20
17	CdF_2 In-Sn, PS-2 In_2O_3	2.80	1.79	0.4	1.23	1.20
18	In_2O_3 In-Sn, PS-2	2.78	1.46	0.4	0.77	0.78



Cathode No.	Type	Current Density (ma/cm^2)	Current Density (ma/g CdF$_2$)	Theoretical Discharge Time (hr)
5	CdF$_2$, <40 μm	0.4	5.1	73
7	CdF$_2$, heavy loading, excess In-Sn	0.8	2.9	124
17	CdF$_2$ + In$_2$O$_3$	0.4, 0.9	5.7, 12.8	29 from start
18	In$_2$O$_3$ without CdF$_2$	0.4	-	-

Figure 12. Long-Term Discharge Curves for Several CdF$_2$ Cathodes

Because the effect of the indium oxide additive was discovered near the end of the program, it could not be fully investigated. Some further comment on its effect may be appropriate, however. Since this material was used in the presence of elemental indium, it may have acquired electronic conductivity by infusion of the parent metal. The electrode preparations also contained In-Sn solder, and small quantities of both metals must have been oxidized when the electrodes were hot-pressed in air. Glassy mixtures of In_2O_3-SnO_2 can have resistivities as low as 1.8×10^{-4} ohm-cm.(28) By comparison, graphite, which is a common electrode component, has a resistivity of 1.4×10^{-3} ohm-cm. From these considerations, it appears that the improved performance of the cadmium fluoride could have been due to indium-tin oxide contacts which were more abundant in the presence of excess In_2O_3 powder than in the solder formulations alone. A systematic investigation of low-resistivity In_2O_3-SnO_2 as an additive for CdF_2 and other semiconductive cathode materials would be of interest. For battery electrode development, the active ingredient would, of course, be polycrystalline, rather than single-crystal material.

In Table 7, the performance of the CdF_2-In_2O_3 system, determined from these initial measurements, is compared with that of Ni_3S_2 in a more fully developed battery plate structure.(8) At similar potentials and utilization efficiencies, the cadmium fluoride electrode was discharged in approximately twice the time required for nickel sulfide. With optimization of the plate composition and structure, the CdF_2 system should prove competitive with Ni_3S_2 for organic-electrolyte batteries.

V. CONCLUSIONS

Research on semiconductor cathode materials for ambient-temperature lithium cells was begun at Atomics International in 1967 under sponsorship of the Air Force Cambridge Research Laboratories. Through the intervening time, this work has resulted in five formal reports(1-5) and three technical publications.(29-31) At the completion of the present contract, it is appropriate to summarize the most important results and conclusions derived in this and prior contract periods:

TABLE 7
COMPARISON OF SEMICONDUCTIVE CdF_2 AND Ni_3S_2(8) CATHODES

Cathode Components	Formation Pressure (psi)	Electrolyte	Theoretical Capacity (ma-hr/cm^2)	Current Density (ma/cm^2)	Avg. Cell Potential (v vs Li/Li$^+$)	% Utilization
Ni_3S_2 Al	1800	1 M $LiClO_4$ in THF	55	2.5 4	~ 1.2 ~ 1.2	48[a] 41[a]
CdF_2 In_2O_3 In-Sn	~ 35	0.1 M $TMA \cdot PF_6$ in PC	25	0.9[a]	1.1	38

[a] To 0.90-v cutoff

[b] Discharged 3 hr at 0.4 ma/cm^2, followed by 9.5 hr at 0.9 ma/cm^2

1. The cathode performance of cadmium fluoride in organic electrolytes is improved by its conversion to an n-type semiconductor. Porous plates formulated with the conductive material compare favorably with those containing nickel sulfide.

2. The enhanced reactivity of n-type CdF_2 is due to a discharge mechanism involving the electronic charge carriers.(29, 30) This mechanism is identified by formation of the metallic discharge product at the interface between the semiconductor and the electrolyte solution. In contrast, a solid ionic conductor will produce a discharge product at its boundary with the electronic current collector, while a soluble cathode reactant will be discharged at the current collector/solution interface.

3. For some cathode systems, the discharge mechanism involving a partially soluble reactant can occur in parallel with a solid state mechanism. Discharge through the solution process may be controlled by the rates of dissolution and diffusion of the reacting material. A mathematical model was developed for a partially soluble cathode material and verified by measurements in a thin-layer electrochemical cell.(31)

4. The electronic discharge mechanism with CdF_2 in PC can lead to passivation of the semiconductor surface, apparently by LiF, when lithium ions are present.(4, 30) This was prevented by using a lithium-free electrolyte, TMA·PF_6-PC. The cadmium fluoride could then be discharged to a depth of 68 μm before a decline in voltage occurred. The discharge appeared to be limited, finally, by the accumulation of porous cadmium metal on the CdF_2 surface.

5. Single-crystal cathodes of n-type CdF_2 provide a standard of cathode performance that can be approached, but probably not surpassed, by the same material in porous form, when due allowances are made for true surface areas and thickness of the material utilized.

6. Successful use of a high energy-gap semiconductor as a battery cathode material depends on the formation of good electronic contacts throughout the porous electrode structure. A systematic approach to the selection of current collectors was developed, with attention to the work function of the

additive, such as carbon or a metal, and the electron affinity of the semiconductor. Several additives for cadmium fluoride were investigated on this basis. A formulation consisting of CdF_2 and In_2O_3 with In-Sn solder proved most effective.

7. It was known before this investigation that cadmium fluoride could be converted to an n-type semiconductor by a two-stage doping procedure.(27) N-Type zinc fluoride with a room-temperature resistivity near 0.5 ohm-cm was produced in the course of this research by fusing the salt with excess zinc in the absence of air.(3) Although the resulting material had low electrochemical reactivity under the testing conditions used, it was about 100 times more conductive than zinc fluoride preparations previously described in the literature.

8. Areas recommended for further work include:

   a) Improvement of the formulation and structure of porous cadmium fluoride battery plates.

   b) Investigation of electronic contacts in a variety of semiconductive battery cathode materials, including selected fluorides, sulfides, and oxides.

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