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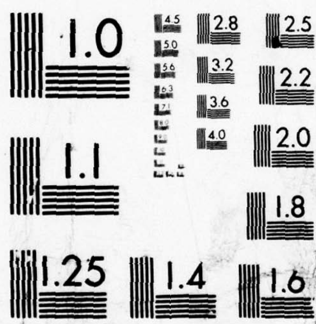

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The manuscript presents an overview of the composition, structure, mechanical properties and electrochemical behavior of chromium containing alloys used in the fabrication of dental, maxillofacial and orthopedic prostheses.

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BASE METAL DENTAL AND SURGICAL ALLOYS

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WASHINGTON, D. C. 20012

BASE METAL DENTAL AND SURGICAL ALLOYS

Dr. Eugene F. Huget and Dr. Stanley G. Vermilyea

The use of cobalt-chromium and nickel-chromium alloys for the fabrication of dental and skeletal prostheses has grown markedly over the past three decades. A combination of features such as low cost, alleged resistance to corrosion, high strength and rigidity and low density has made these substances attractive alternatives to other available materials.

In dentistry, castable chromium type alloys are the principal materials from which removable partial denture frameworks are constructued. They are used to a lesser extent in the fabrication of full denture bases, subperiosteal and endosseous implants, tooth-borne surgical splints and permanent fixed prostheses (crowns and bridges).

Medical-surgical applications of chromium containing prostheses are numerous. Devices such as pins, screws, plates and meshes are especially useful in the fixation of fractured bones. Cast prostheses of more complicated design are used in the repair of diseased and damaged joints (total hip prostheses), for the internal fixation of facial fractures, for the repair of contour defects of the face and skull and for reconstruction of the mandible.

ALLOY COMPOSITION

The compositions of 22 chromium containing alloys are given in Table 1.[1-10] Materials A through I are used primarily for the routine centrifugal casting of the rigid major and minor connectors of removable partial dentures. Materials J through R are tailored for the precision casting of fixed dental restorations. Devices cast from alloys S and T are used as dental, maxillofacial and orthopedic implants. Alloy U is an implantable surgical grade austenitic stainless steel. Material V is a wrought surgical alloy.

To meet the present composition requirement of American Dental Association Specification No. 14, base metal partial denture alloys must contain a total of not less than 85 percent by weight of chromium, cobalt and nickel.[12] Such alloys are considered capable of exhibiting a reasonable degree of resistance to the corrosive environment of the oral cavity.

Cobalt and chromium are the major components of most partial denture casting alloys. These materials are strengthened and hardened by minor additions of molybdenum, iron, tungsten, manganese and carbon. A significant departure from the use of cobalt as a major alloying element is reflected by the compositions of alloys H and I (Table 1). These materials are based on a nickel-chromium system. Important minor constituents of the nickel-chromium alloys include aluminum and beryllium. Aluminum and nickel form a gamma prime (γ') phase on cooling of the alloys from their solidus to room temperature.

Presumably, γ' is an intermetallic compound (Ni_3Al)[3,12] Formation and precipitation of γ' aid in strengthening and hardening of these nickel-rich alloys.[2,12,13] Beryllium contributes to the lowering of the fusion temperature range and to the refinement of grain structure.

More than 20 base metal alloys have been marketed for use in fixed prosthodontic procedures. These materials are used mainly for the fabrication of rigid substructures to which esthetic porcelain veneers can be fused. Nickel, about 60 to 80 percent by weight, and chromium, about 12 to 20 percent by weight, are the major components of most available products. Modification of the highly versatile nickel-chromium system by addition of varying amounts of other elements such as aluminum, molybdenum, manganese, tungsten, niobium, boron, silicon, beryllium and carbon has made possible the availability of a broad selection of castable alloys, the structural features, properties and handling characteristics of which are significantly diverse.

Compositions of the surgical alloys (Table 1, materials S through V) exhibit striking differences. Specifications for these materials are the responsibility of the American Society for Testing and Materials Committee F-4 for Surgical Implants.[14-17]

Compositional features of the surgical grade alloys merit special consideration. In time, and while implanted in living tissue, ionization of the components of any alloy can occur regardless of alleged corrosion resistance.[18] Constituent elements of implant alloys have been detected in local tissues and in distant target organs, particularly the lungs and spleen. The severity of the reaction of living tissue to any surgically implanted device will depend upon the concentration and cytotoxic potentials of ions made available through dissolution of products produced by wear and corrosion of the implant's surface.

ALLOY MICROSTRUCTURE

The microstructure of a typical cobalt-chromium alloy is shown in Figure 1. For the most part, the structures of the cobalt-based materials are typified by a cored austenitic solid solution matrix and isolated lamellar carbides. The conditions under which certain specific compositions are cast, however, may lead to the deposition of filamentous carbides along grain boundaries or the formation of discontinuous carbides.[19]

The microstructures of four nickel-chromium based alloys used in fixed prosthodontic procedures are shown in Figure 2. Subtle as well as obvious differences exist among the depicted structures. The microstructure of Alloy J is characterized by slender carbides which partially delineate grain boundaries. Additionally, a relatively coarse dispersion of an intragranular precipitate (presumably Ni_3Al) is located adjacent to the boundary areas. The intragranular regions of Alloy K are devoid of observable precipitates. Grain boundaries of Alloy K are demarked by discontinuous spherical carbides. The cored dendrites and continuous grain boundary phase of Alloy L are more typical of cobalt-chromium alloys than of the other available nickel-chromium based materials. The structure of Alloy M, a boron containing material, exhibits a prominent and abundant dendritic precipitate.

PHYSICAL AND MECHANICAL PROPERTIES

The fusion temperature ranges of cobalt-chromium and nickel-chromium alloys are significantly higher than those of gold based casting alloys. A melting temperature of 1,399°C to 1,454°C is common. In the fabrication of dental prostheses, high fusion temperature ranges offer both advantages and disadvantages. Alloys intended for use with fused porcelain must be capable of withstanding the temperatures (≃1010°C) at which the porcelain is fired. Substructures cast from nickel-chromium alloys exhibit greater ability to resist sag and distortion during the porcelain firing procedure than those cast from gold-platinum-palladium alloys. However, since the chromium type alloys are cast at very high temperatures, their shrinkage from liquidus to solidus is greater than that of dental golds. Although extensive data on the shrinkage of gold alloys are available, sufficient information relevant to the shrinkage of the base metal alloys is lacking. Elevated fusion temperature ranges preclude the use of conventional ovens for mold burnout as well as the employment of simple and inexpensive casting equipment.

Densities of the base metal partial denture, crown-and-bridge and surgical casting alloys lie in the vicinity of 8 gm per cc. The weight of a prosthesis cast from a chromium type alloy would be approximately one-half that of a comparable appliance cast from a gold alloy.

The available base metal alloys offer a relatively broad range of mechanical properties. Some as-cast characteristics of seven base metal alloys are presented in Table 2.[2,4,5,8,13] It must be pointed out that the tabulated property values were obtained from experiments conducted in one laboratory. Because of variations in techniques of spruing, pattern investment, mold burnout and casting that exist among laboratories, data on these materials from another testing facility might be somewhat different.

Generally speaking, the nickel-chromium and cobalt-chromium alloys exhibit strengths comparable to those of hardened gold containing partial denture alloys. The base metal partial denture and crown-and-bridge alloys, however, are approximately twice as rigid as their gold alloy counterparts. Although conclusions based on comparison of hardness values for multiphase base metals with hardness values for single phase gold alloys may be misleading, the hardness of the chromium type materials would appear to be about one-third greater than that of dental golds used for the same purpose.

High modulus of elasticity of the base metal casting alloys makes possible the design and clinical use of relatively thin dental and surgical prostheses.

ELECTROCHEMICAL BEHAVIOR

The suitability of certain base metal alloys for use as dental and biomedical materials is predicated upon the ability of chromium to resist corrosion and tarnish by its passivating effect. Experience has shown, however, that corrosion of prostheses fabricated from chromium type alloys can occur.[18,20-23]

Surfaces of alloys subjected to abusive environments may undergo several types of electrochemical dissolution. Dental and biomedical applications of metallic substances require careful consideration of the probability of the occurrence of (1) galvanic interaction of dissimilar metals, (2) stress corrosion, (3) crevice corrosion and (4) pitting. The effects of galvanic interaction can be minimized or avoided completely by insuring that all portions of multiple component prostheses be fabricated from the same alloy. Prudent surgical practice further requires that implants and instruments used for their insertion be cast not only from the same alloy, but also of ingots from the same lot. For the most part, yield assisted (stress) corrosion can be precluded by selection of materials exhibiting suitable mechanical properties.

The juxtapositional relationship of metallic prostheses and living tissues creates crevices which encourage electrochemical attack (crevice corrosion). In clinical practice many of the conditions responsible for initiation and propagation of crevice corrosion can not be avoided. On the other hand, the occurrence of pitting, a somewhat different electrochemical phenomenon, appears to depend mainly on the specific compositional and structural features of certain alloys.[24]

Electrochemical laboratory techniques have been used for many years to investigate the localized corrosive attack which occurs on base metal biomedical alloys exposed to chloride media.[9,25,26] Unfortunately, definitive correlation of in vitro observations to clinical performance capability is not entirely possible.

Cyclic potentiodynamic polarization plots of a few chromium containing alloys are presented in Figures 3-8. The corrosive medium to which the alloys were exposed was a lactated Ringer's solution (chloride ion conc. 109 m Eq per liter). Temperature of the test solutions was 37°C. The anodic scans depict transition from a metastable to an active condition and subsequently delineate the active[a], passive[b] and transpassive[c] ranges of the materials. Corrosion potential[d] is marked by intersection of the anodic (oxidation) and cathodic (reduction) curves. Additional relationships of the paired curves yield other information relevant to the electrochemical behavior of an alloy immersed in a corrosive medium. Figures 3-6 reveal a distinct hysteresis between the anodic and cathodic components of the cyclic potentiodynamic polarization diagrams. On the other hand, the diagrams shown in Figures 7 and 8 exhibit little or no hysteresis.

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a Marked increase in current density with little or no increase in impressed anodic potential.

b Little or no change in current density with the increase of impressed anodic potential.

c Breakdown of passivity as denoted by Ec.

d Potential at which the rate of oxidation is equal to the rate of reduction as denoted by Ecorr.

It has been suggested that metallic substances displaying a marked hysteretic tendency upon cyclic polarization are particularly susceptible to pitting corrosion.[24] Presently, however, the extent to which dissolution by pitting would affect the long term mechanical performance and biocompatability of certain base metal surgical and dental alloys is unknown and remains to be studied.

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TABLE 1

COMPOSITION OF BASE METAL DENTAL AND SURGICAL ALLOYS

Alloy	Co(%)	Ni(%)	Cr(%)	Mo(%)	Fe(%)	Si(%)	W(%)	Mn(%)	Cu(%)	Be(%)	Al(%)	C(%)	Other
A[a]	43.5	20.1	21.6	7.0	0.25	0.35	--	3.0	3.5	0.9	--	0.05	--
B[a]	59.4	1.5	30.3	5.8	0.70	0.55	0.35	0.34	--	--	--	ND[b]	--
C[a]	29.7	0.7	22.3	3.3	40.0	1.7	--	0.9	--	--	--	ND[b]	--
D[a]	62.6	2.3	26.2	5.0	1.0	0.55	1.2	0.16	0.20	--	--	0.25	--
E[ac]	61.5	2.3	27.6	5.3	1.6	X[d]	--	0.8	--	--	X[d]	X[d]	--
F[ac]	65.0	--	30.0	4.0	--	--	--	--	--	--	--	--	?[e]
G[f]	51.6	15.5	26.7	3.7	1.2	0.44	--	0.57	0.08	--	--	0.23	--
H[f]	0.5	70.7	16.0	3.7	0.96	0.44	0.60	3.50	0.04	1.20	2.30	0.05	--
I[g]	0.9	70.4	16.1	4.0	0.75	0.42	0.65	3.77	0.01	0.48	2.45	0.30	--
J[g]	0.9	70.0	16.0	4.1	0.78	0.48	0.85	3.84	0.01	0.46	2.55	0.30	--
K[h]	--	79.0	11.0	3.6	0.05	1.10	--	--	0.02	--	1.75	0.09	Nb[i]
L[j]	0.01	76.0	13.8	4.6	1.50	1.11	--	0.09	--	--	2.80	0.05	--
M[h]	0.01	69.9	19.9	5.6	0.12	1.06	--	0.01	--	--	--	0.22	B[k]
N[l]	9.3	60.0	15.0	2.1	0.21	0.65	--	--	0.03	--	3.0	0.14	Nb, Ti[m]
O[l]	0.1	61.5	22.4	9.95	0.35	0.86	--	0.20	0.06	--	--	0.10	Nb[n]
P[j]	0.2	70.6	15.7	4.50	0.23	1.54	--	3.20	--	--	3.80	0.12	--
Q[o]	0.3	67.5	19.7	4.20	0.07	3.0	--	1.20	1.85	--	--	0.13	Sn[p]
R[o]	--	79.9	12.4	2.0	0.13	0.16	--	0.12	0.13	2.10	2.80	0.25	--
S[q]	61.1	0.3	31.6	4.4	0.58	0.63	--	0.71	0.01	--	0.01	0.40	--
T[q]	15.4	54.3	24.6	4.3	0.71	0.45	--	0.03	0.03	--	0.02	0.01	--
U[r]	--	11.4	17.1	2.3	67.70	--	--	1.50	--	--	--	0.03	--
V[s]	34.8	10.1	21.5	0.56	2.23	0.50	15.9	1.32	0.05	--	12.7	0.11	--

Continuation of TABLE 1

a Taylor, D. F., Leibfritz, W. A., and Adler, A. G., J.A.D.A. 56, 343 (1958).

b Not determined.

c Reported by manufacturer

d Reported as total Si, Al and C.

e Unspecified additiona.

f Civjan, S., Huget, E. F., Reinke, P. E., and Pierce, S. W., IADR Program and Abstracts, paper No. 311 (1971).

g Civjan, S., Huget, E. F., and Lichtenberger, H., IADR Program and Abstracts, paper No. 540 (1970).

h Huget, E. F., Vilca, J. M., and Wall, R. M., IADR Program and Abstracts, paper No. 642 (1977).

i Nb 3.2%.

j Huget, E. F., Dvivedi, N., and Cosner, H. E., Jr., J.A.D.A. 94, 87 (1977).

k B 2.90%.

l Huget, E. F., and Vermilyea, S. G., unpublished data.

m Nb 4.9% and Ti 4.0%.

n Nb 4.3%.

o Huget, E. F., Civjan, S., and Dvivedi, N. N., IADR Program and Abstracts, paper No. 733 (1974).

p Sn 2.0%.

q Civjan, S., Huget, E. F., Erhard, W. L., and Vaccaro, G. J., Oral Surg. 28, 77 (1972).

r Cahoon, J. R., Bandyopadhya, R., and Tennese, L., J. Biomed. Mater. Res. 9, 250 (1975).

s Huget, E. F. and Civjan, S. unpublished data.

TABLE 2

PROPERTIES OF BASE METAL CASTING ALLOYS

Alloy[a]	Tensile Strength MN/m^2	Yield Strength (0.2% Offset) MN/m^2	Elastic Limit MN/m^2	Young's Modulus X10^3 MN/m^2	Elongation %	Hardness Rockwell 30 N
G[b]	670	495	395	230	8	50
I[c]	900	770	665	215	5	51
K[d]	640	585	475	215	1	42
L[e]	460	445	385	185	2	33
M[d]	750	525	290	185	1	50
S[f]	895	690	475	248	2	54
T[f]	470	330	260	200	20	20

a Compositions presented in Table 1

b Civjan, S., Huget, E. F., Reinke, P. E., and Pierce, S. W., IADR Program and Abstracts, paper No. 311 (1971).

c Civjan, S., Huget, E. F., Godfrey, G. D., Lichtenberger, H., and Frank, W. A., J. Dent. Res. 51, 1537 (1972).

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e Huget, E. F., Dvivedi, N., and Cosner, H. E., Jr., J.A.D.A. 94, 87 (1977).

f Civjan, S., Huget, E. F., Erhard, W. L., and Vaccaro, G. L., Oral Surg. 28, 77 (1972).

LEGENDS FOR FIGURES

Figure 1. Structure of a cobalt (51.6 percent)-chromium (26.7 percent)-nickel (15.5 percent) partial denture alloy. Original magnification 450 X.

Figure 2. Structures of four nickel-chromium crown-and-bridge alloys. Original magnification 450 X. Compositions of the alloys are given in Table 1.

Figure 3. Anodic and cathodic polarization plots for a nickel-chromium partial denture alloy (Table 1, Alloy I). Chloride ion concentration of the test medium was 109 m Eq per liter.

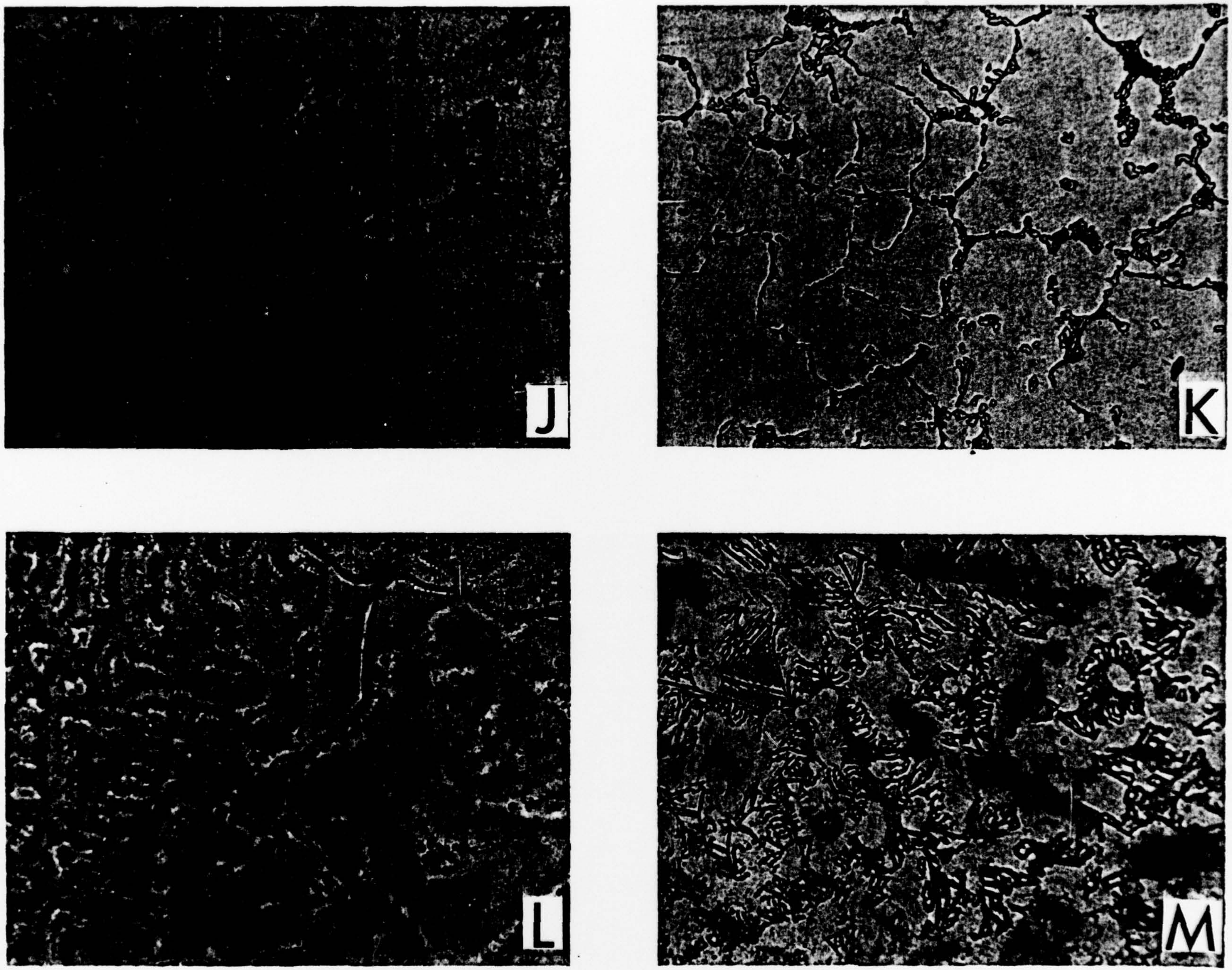
Figure 4. Anodic and cathodic potentiodynamic polarization plots for a nickel-chromium crown-and-bridge alloy (Table 1, Alloy L). Chloride ion concentration of the test medium was 109 m Eq per liter.

Figure 5. Anodic and cathodic potentiodynamic polarization plots for a boron containing nickel-chromium based crown-and-bridge alloy (Table 1, Alloy M). Chloride ion concentration of the test medium was 109 m Eq per liter.

Figure 6. Anodic and cathodic potentiodynamic polarization plots for a surgical grade stainless steel. Specific composition of the alloy was not determined. Chloride ion concentration of the test medium was 109 m Eq per liter.

Figure 7. Anodic and cathodic potentiodynamic polarization plots for a cobalt-chromium-molybdenum surgical casting alloy (Table 1, Alloy S). Chloride ion concentration of the test medium was 109 m Eq per liter.

Figure 8. Anodic and cathodic potentiodynamic polarization plots for a nickel based surgical casting alloy (Table 1, Alloy T). Chloride ion concentration of the test medium was 109 m Eq per liter.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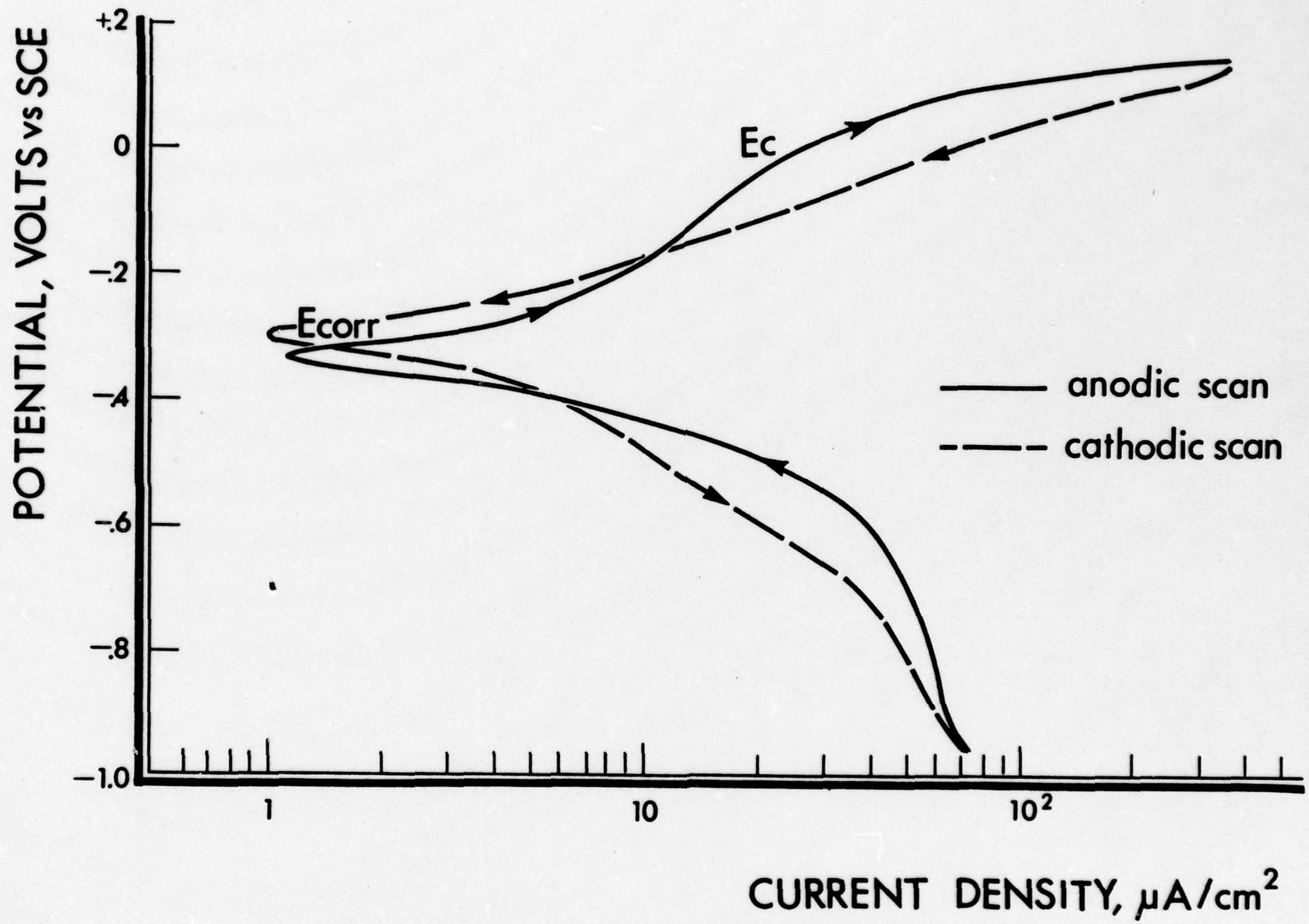
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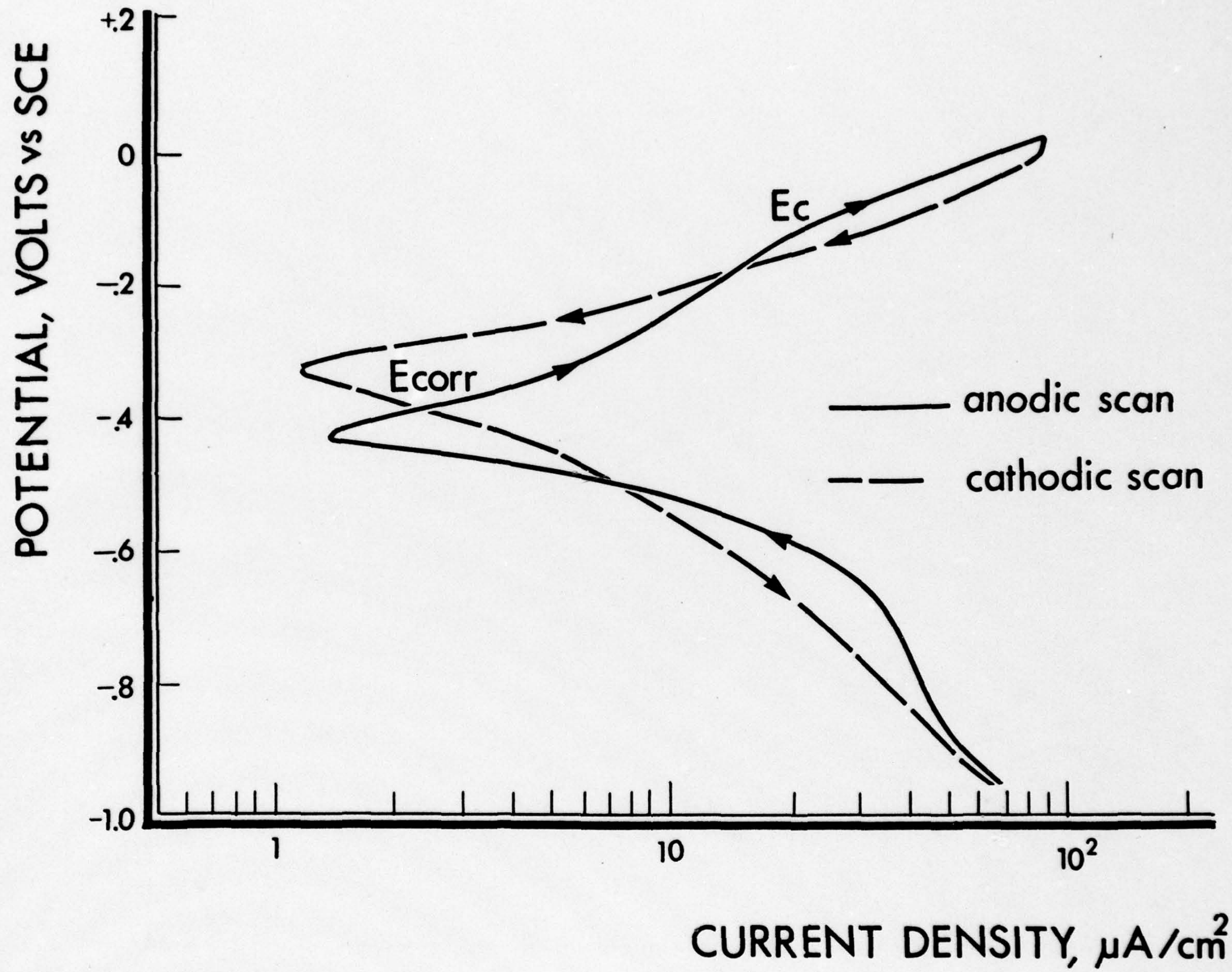
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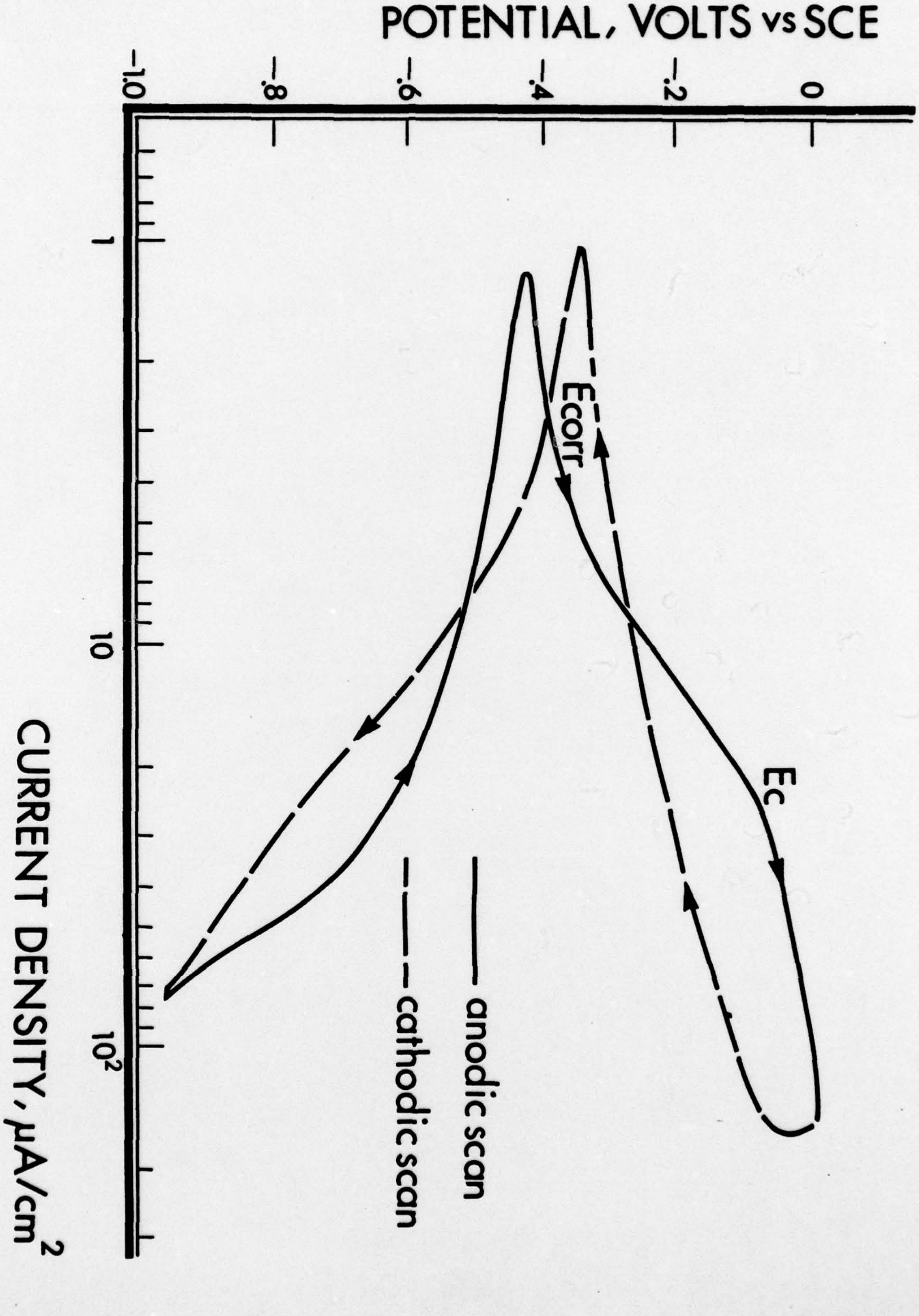

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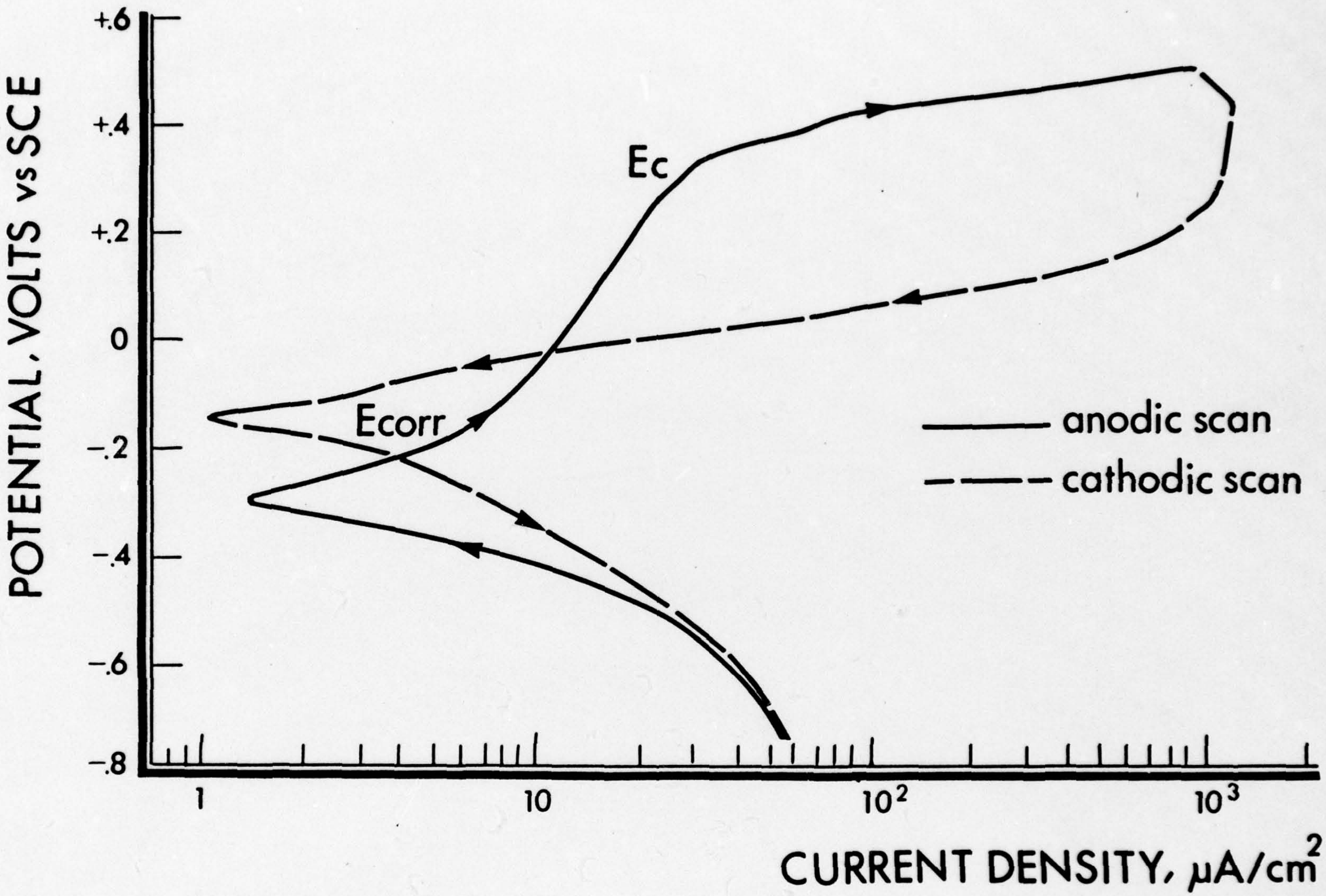

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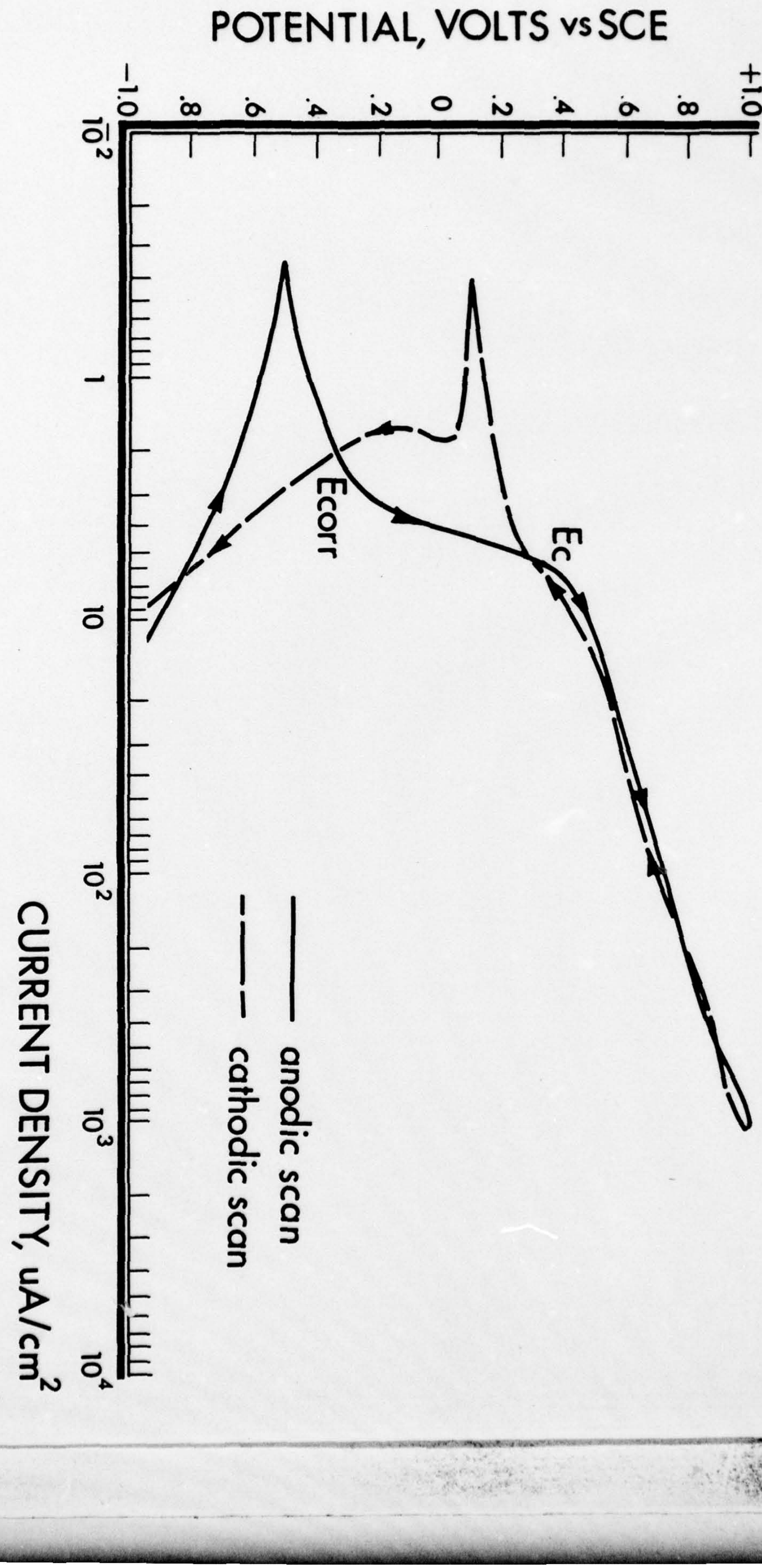

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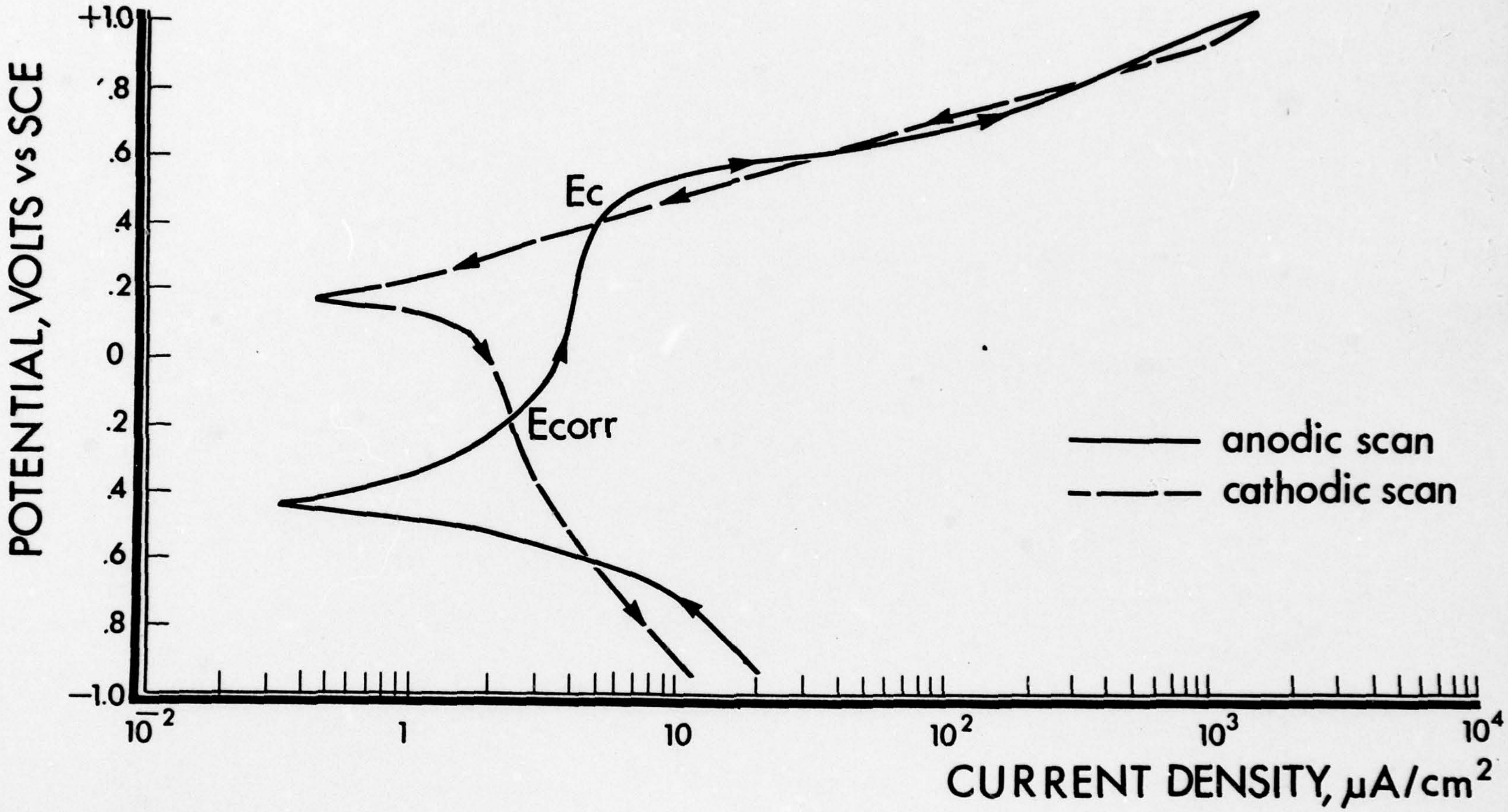

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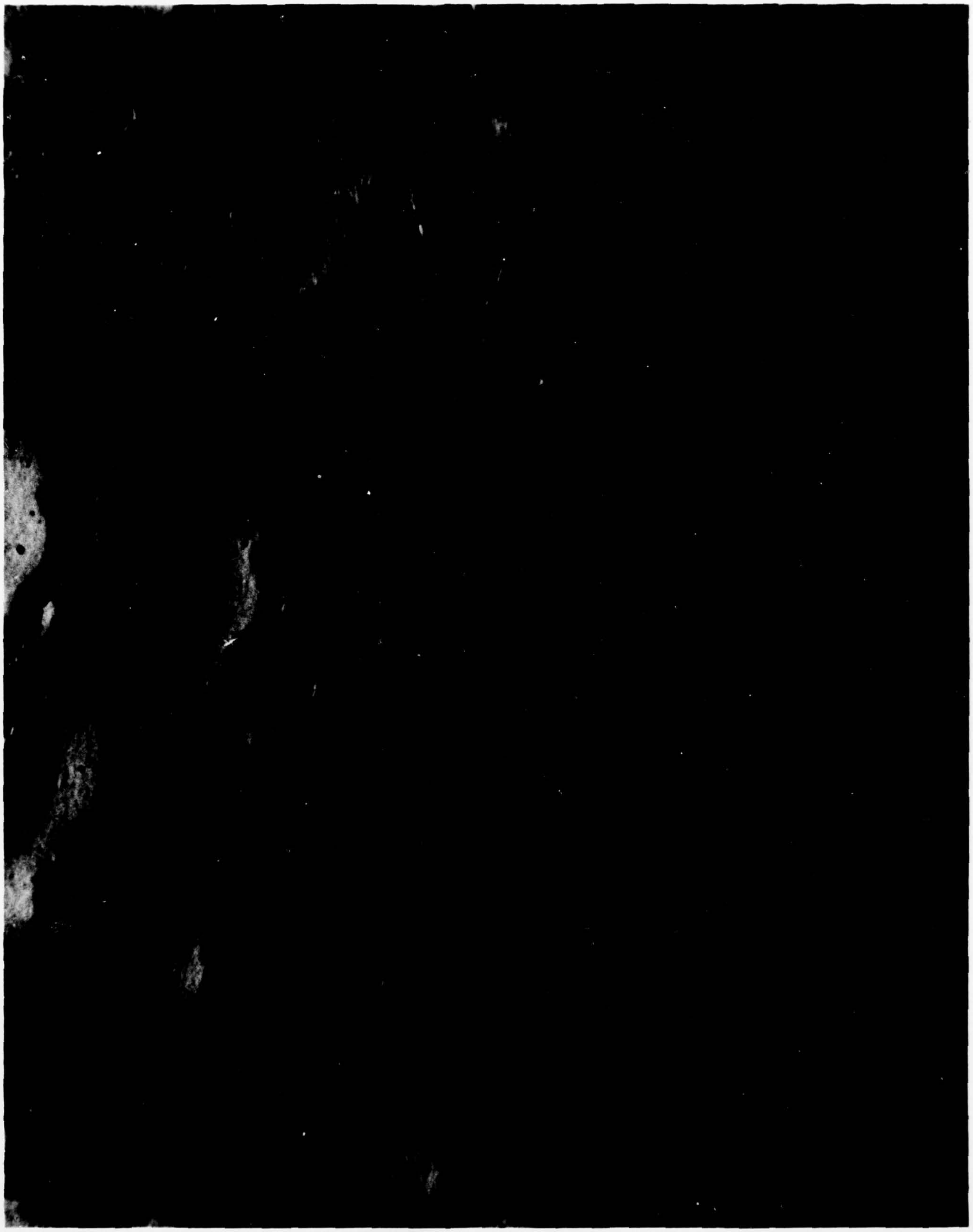
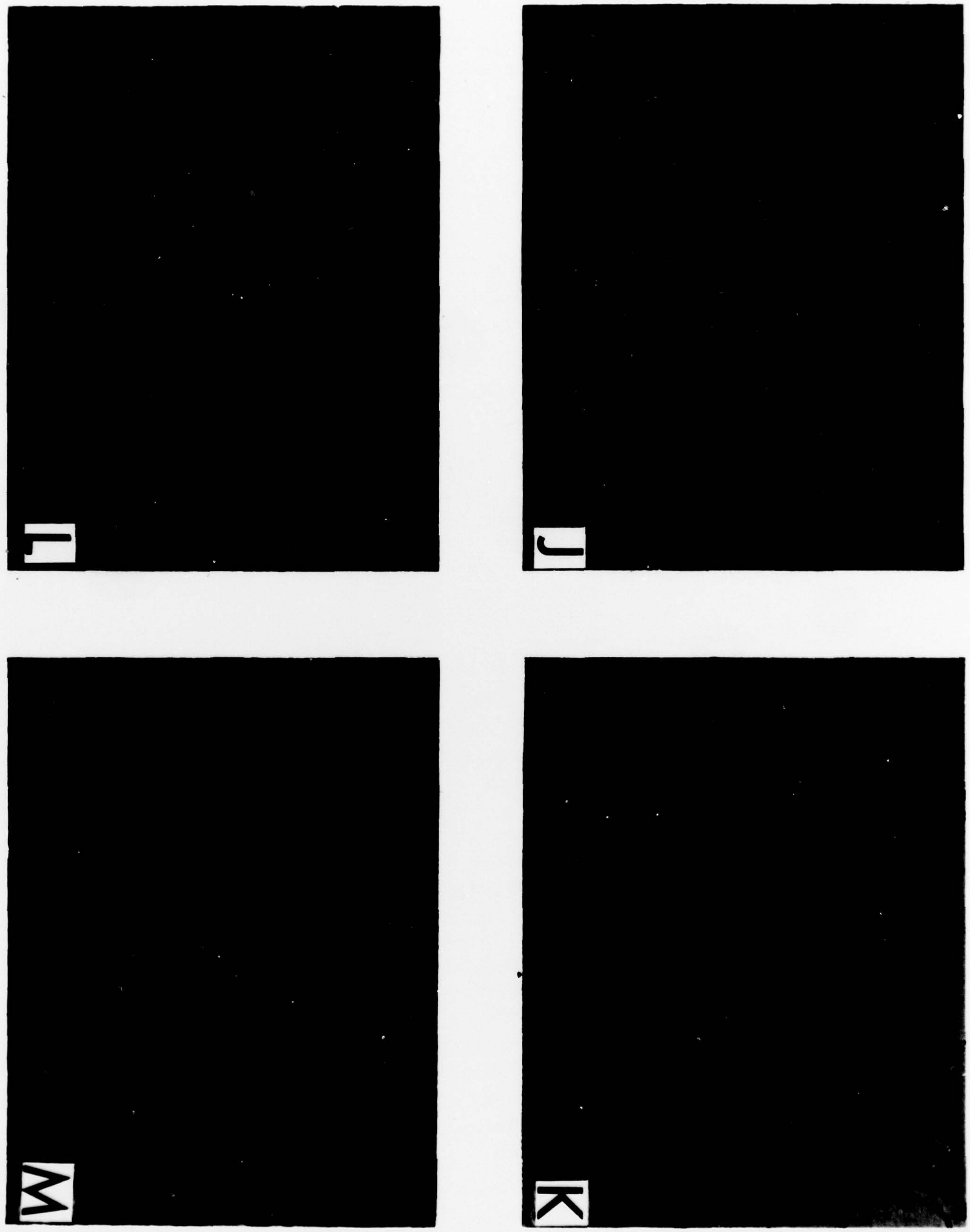
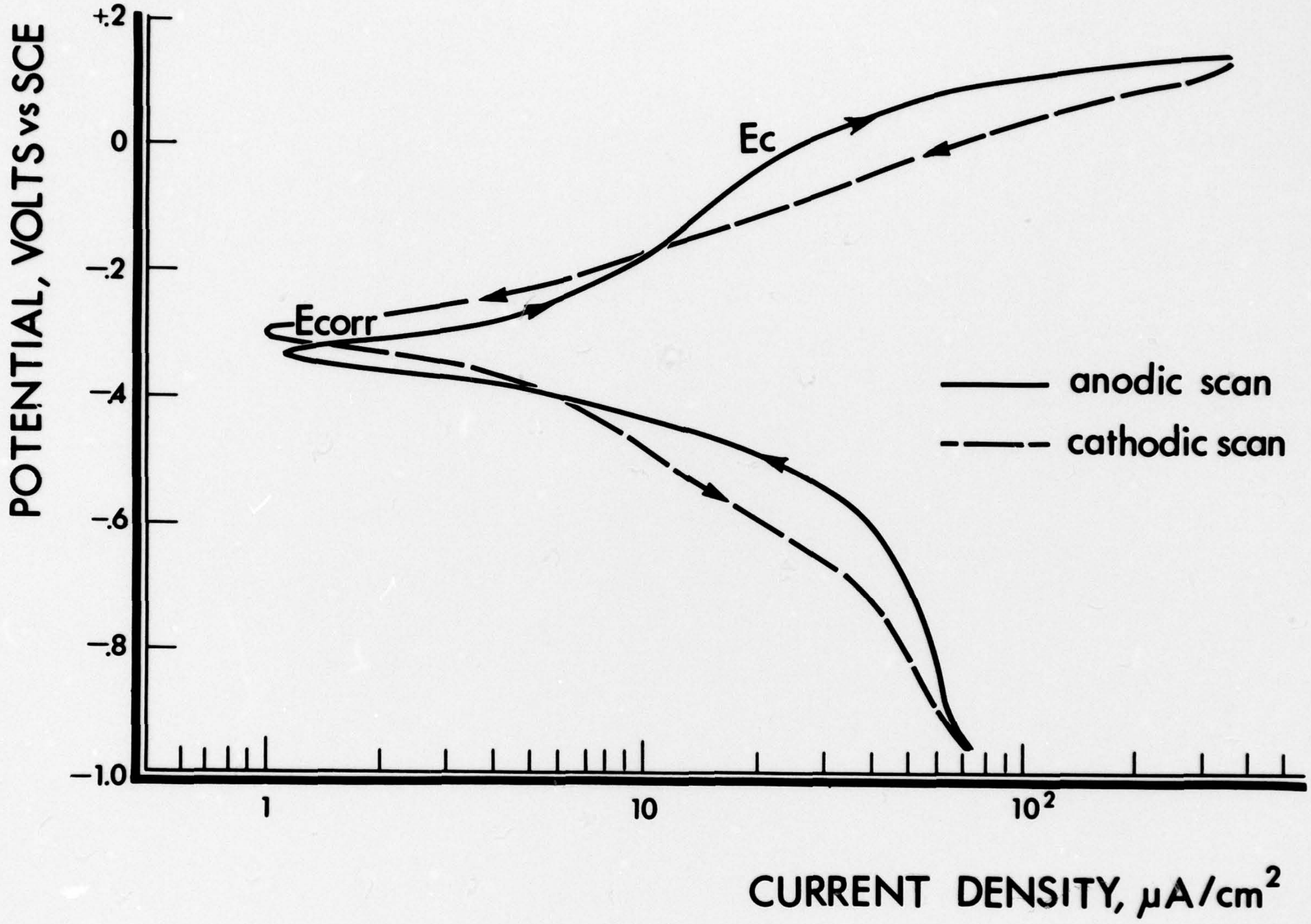
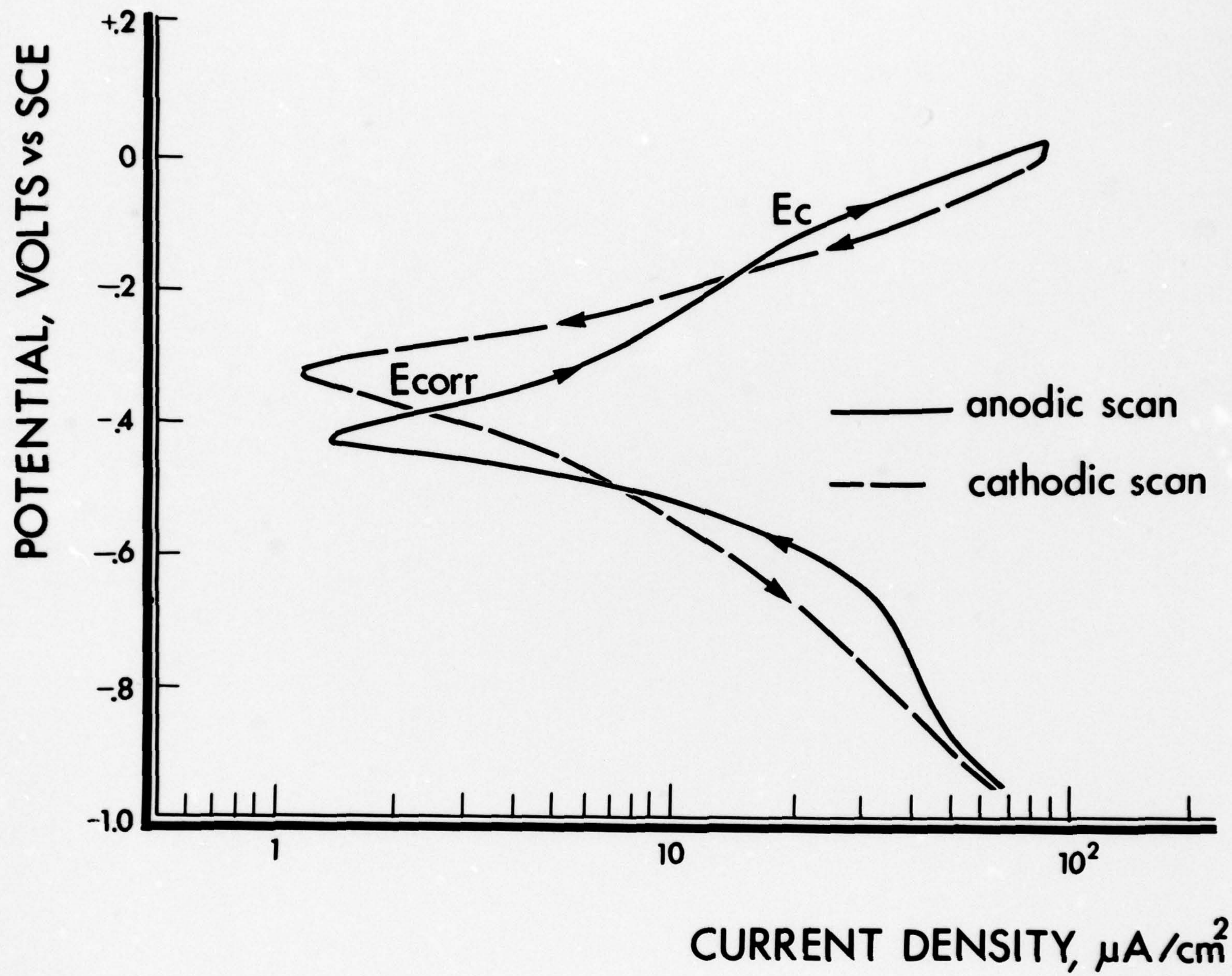
anodic scan
cathodic scan



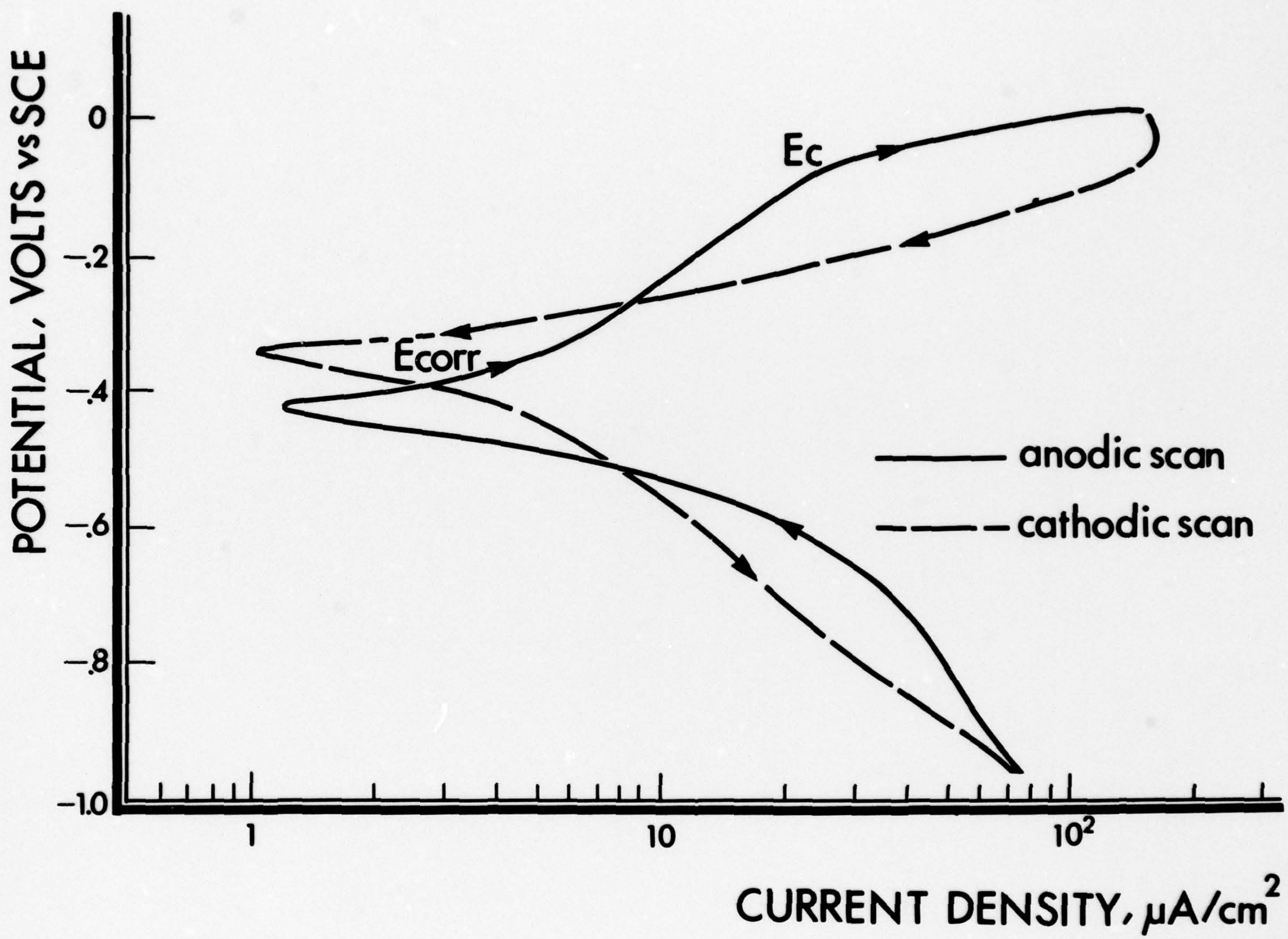


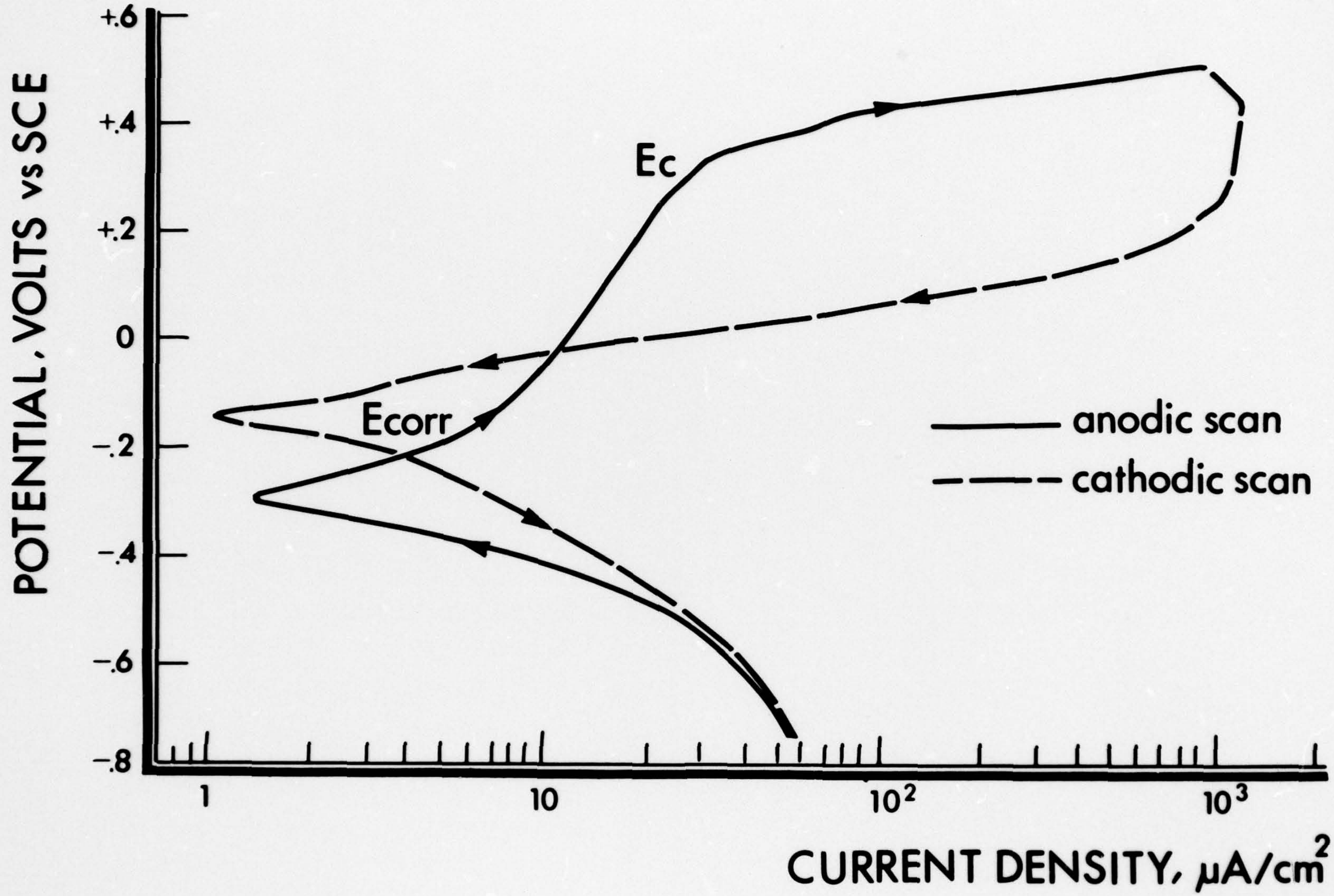
L
J
M
K

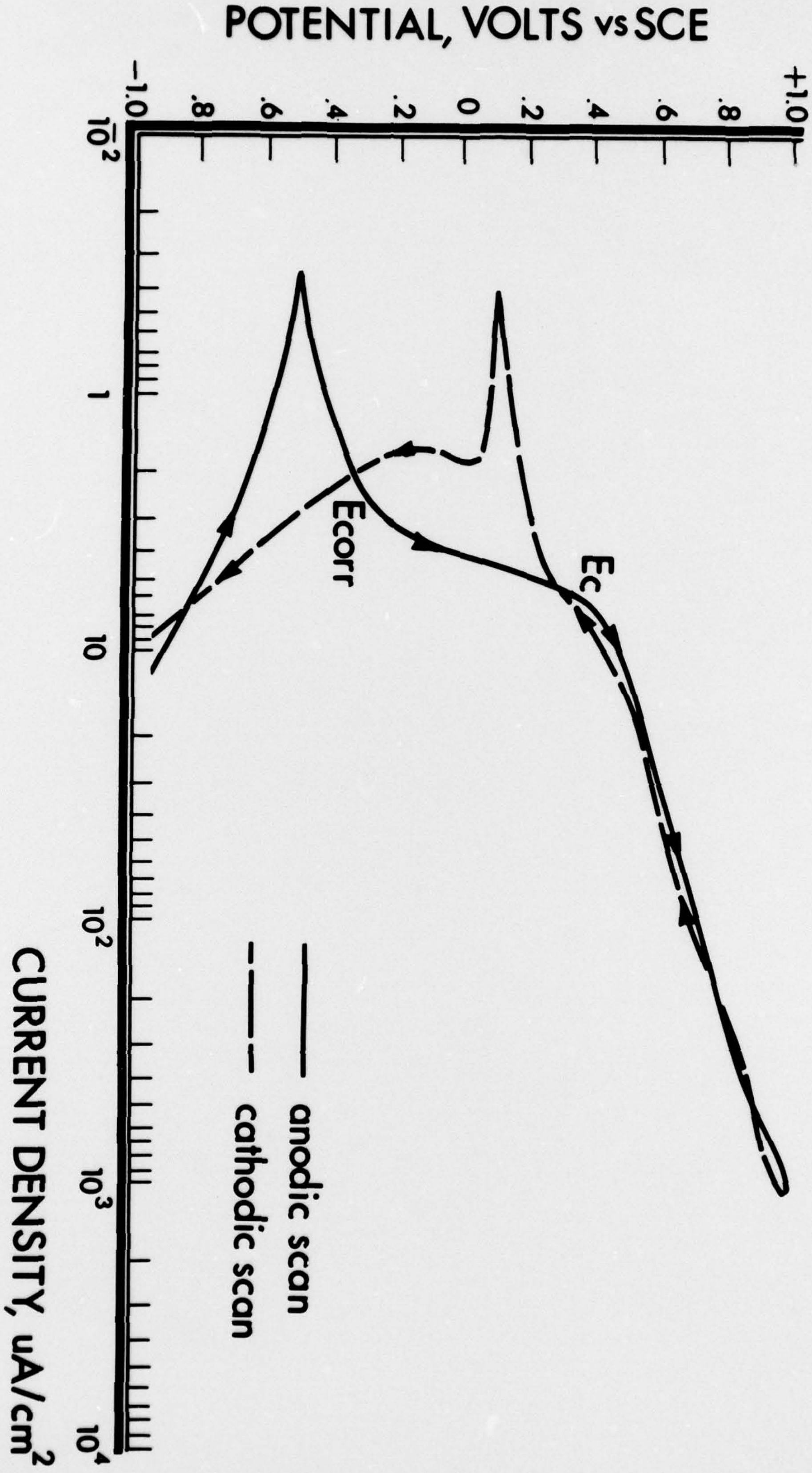

POTENTIAL, VOLTS vs SCE
+.2
0
-.2
-.4
-.6
-.8
-1.0
1
10
10²
CURRENT DENSITY, μA/cm²
Ecorr
Ec
anodic scan
cathodic scan



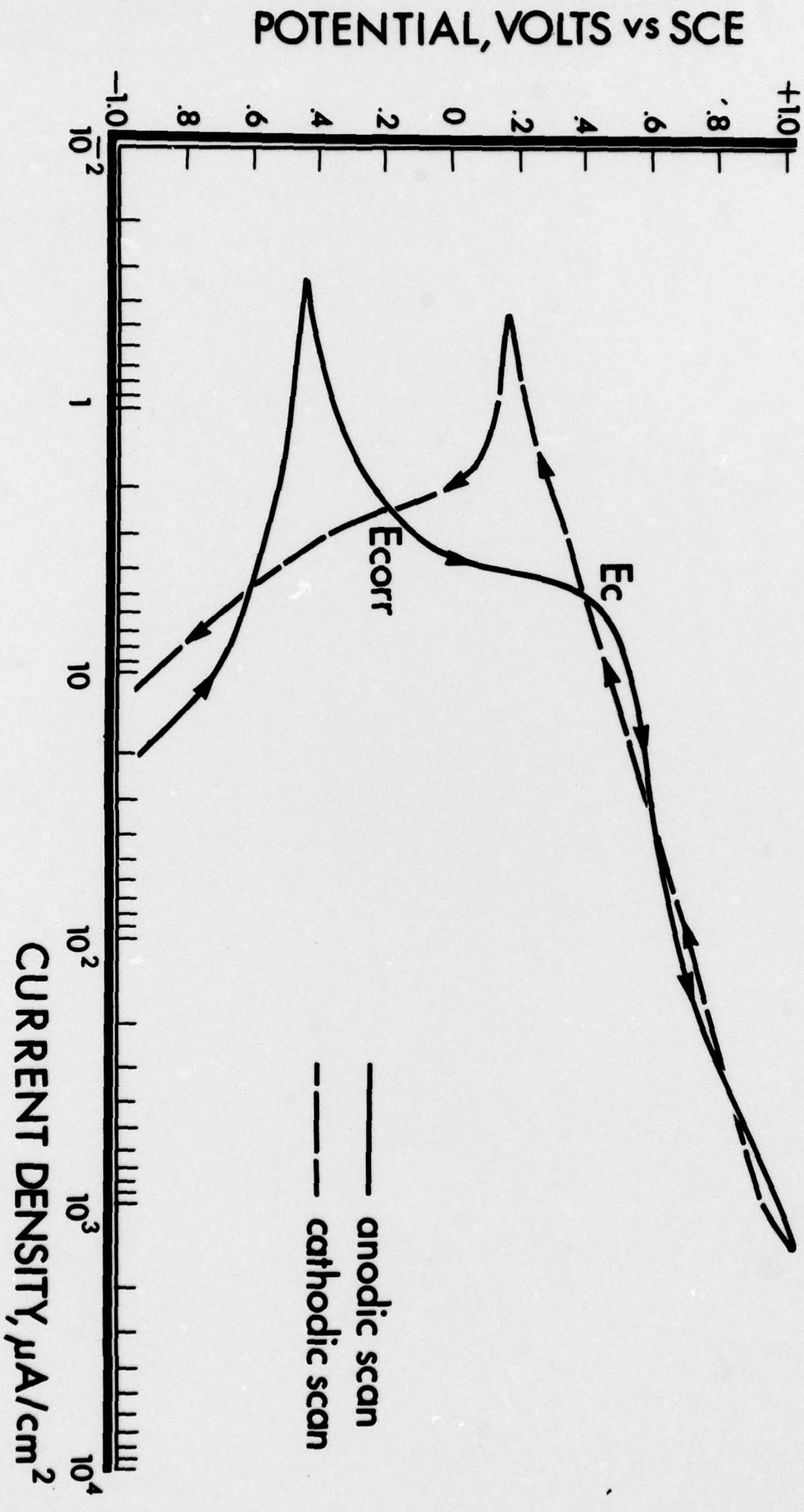
POTENTIAL, VOLTS vs SCE
+.2
0
-.2
-.4
-.6
-.8
-1.0
1
10
10²
CURRENT DENSITY, μA/cm²
Ec
Ecorr
anodic scan
cathodic scan


POTENTIAL, VOLTS vs SCE
0
-.2
-.4
-.6
-.8
-1.0
1
10
10^2
CURRENT DENSITY, $\mu A/cm^2$
Ec
Ecorr
anodic scan
cathodic scan


POTENTIAL, VOLTS vs SCE
+.6
+.4
+.2
0
-.2
-.4
-.6
-.8
Ec
Ecorr
anodic scan
cathodic scan
1
10
10²
10³
CURRENT DENSITY, μA/cm²



POTENTIAL, VOLTS vs SCE
-1.0
.8
.6
.4
.2
0
.2
.4
.6
.8
+1.0
10^{-2}
1
10
10^2
10^3
10^4
Ecorr
Ec
anodic scan
cathodic scan
CURRENT DENSITY, uA/cm^2



POTENTIAL, VOLTS vs SCE
−1.0
.8
.6
.4
.2
0
.2
.4
.6
.8
+1.0
10^{-2}
1
10
10^2
10^3
10^4
Ecorr
Ec
anodic scan
cathodic scan
CURRENT DENSITY, μA/cm^2