

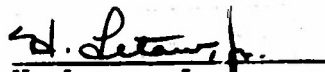
THE ELECTROLYTIC ANALOGUE TRANSISTOR

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1. INTRODUCTION

The operation of both point-contact and junction transistors depends on current flow in semiconductors when carriers of two signs, electrons and holes, are present. For example, in a P-N-P junction transistor, holes injected at one P-N junction, the emitter, diffuse across the narrow N-region to the collector junction. The magnitude of the current depends upon the voltage difference between the emitter and the base electrode which makes a low resistance contact to the N-region. When the collector is biased in the reverse direction, most of the current flowing to the collector comes from the emitter and the current is nearly independent of collector voltage.

We have constructed an electrolytic analogue of the junction transistor in which the flow of ions in solution replaces flow of electrons and holes in the semiconductor. An oxidation-reduction couple forms a suitable system. The ion in the reduced state is analogous to the electron and in the oxidized state to the hole. In the analogue of the P-N-P transistor, the electrolyte is normally in the reduced state. One electrode, the analogue of the base, makes a low resistance contact to the solution. The emitter and collector of the analogue are similar highly polarizable electrodes such that little current flows unless the voltage difference between one of the electrodes (the emitter) and the base exceeds a critical value (the decomposition potential) for oxidation to occur. The collector is maintained at a lower voltage than the emitter and is placed in very close proximity. Oxidized ions released at the emitter diffuse to the collector where the reverse reaction occurs with the return of the ions to the reduced state. If the solution is normally in the oxidized state, one has the analogue of the N-P-N transistor. The polarities are reversed and the reaction occurring at the emitter is a reduction.

If the conductivity of the electrolyte is sufficiently high, the electric fields in solution are small and the ions move mainly by diffusion. Inert electrolytes may be added to increase conductivity.

The frequency response of a transistor is limited by the time taken for carriers to diffuse from the emitter to the collector. In germanium transistors, transit times are of the order of 10^{-7} seconds. Since the mobilities of electrons and holes in germanium are at least 10^7 times larger than those of ions in solution, the transit time in the electrolytic transistor is one second or longer. Transient phenomena which occur in the megacycle range in ordinary transistors occur in the analogue on a greatly expanded time scale and may thus be studied more readily.

It is believed that the analogue may be useful in studying flow problems in transistor structures. The geometrical configuration of electrodes in solution can be changed readily to test a variety of structures. It is not yet certain whether the analogue can be made sufficiently close so that it can be used in a quantitative as well as a qualitative manner.

It is also believed that the electrolytic transistor may have useful applications of its own for current control devices for which ordinary transistors are not suitable.

2. DESIGN OF THE CELL

The base electrode must serve to establish the potential of the solution. The most suitable electrode for this purpose is a relatively unpolarizable one which interacts reversibly with one or more of the ionic species in solution. For example, a mercury pool in contact with mercurous chloride and chloride ion is a satisfactory electrode. The base electrode also serves to maintain the desired oxidation-reduction equilibrium.

In order that transistor action be observed, it is necessary that ionic species produced at one electrode control the current at the other, either through specific participation in the electrode process or else in the rate-determining step. To assure that such action occur in a reasonable time and also to avoid losses through convection or off-axis diffusion, the emitter and collector must be quite close to one another. In the arrangement which we have used, the emitter and collector are circular platinum electrodes 0.5 inch in diameter, one being moved by a micrometer screw arrangement and the other being fixed. The reverse sides of these electrodes are insulated from the solution.

The cell itself is an open framework constructed of lucite which has been properly fabricated and assembled. All joints which come into contact with the solution as well as all submerged metallic parts, except for the tip of the electrical lead to the base electrode and the emitter and collector faces, are thoroughly coated with a suitable cement. As is shown in Fig. 1, the electrical leads are insulated from the solution by being inserted through the cell framework. A piston-cylinder arrangement affords a rather high orientational stability of the movable electrode with respect to the fixed one.

3. EXPERIMENTAL

The circuitry involved in the experimental arrangement was quite standard. Storage batteries were connected through potentiometer rheostats to the emitter and base and collector and base, respectively. Voltmeters and ammeters were connected in the usual way. This, along with the current and voltage convention for P-N-P operation, is shown in Fig. 2.

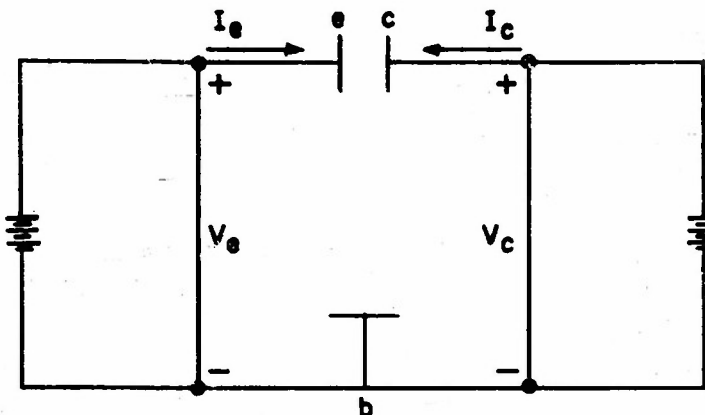


FIGURE 2 CIRCUIT SCHEMATIC AND CURRENT-VOLTAGE CONVENTIONS FOR THE P-N-P ELECTROLYTIC TRANSISTOR

The oxidation-reduction couples utilized in the present research had one property in common, namely that in contact with the calomel half-cell used as ground, the equilibrium concentration ratios of the two species yielded large numbers. It is easily shown that in one of the solutions used, ferrous ion concentration is greater than that of ferric ion by a factor of 10^7 .

In general, the techniques used were simple. A solution of the desired components was prepared and allowed to stand over a mercury pool in a beaker for at least 24 hours. The cell was then placed into the beaker with the desired gross setting of the electrode spacing. No measurements were taken for several hours in order that stirring be allowed to subside. It was found that the device quickly recovered from ordinary vibrations in the laboratory. If the electrodes were spaced less than a few tenths of a millimeter apart, no apparent effects of vibration were observed. This spacing also eliminated interference which could result from thermal or density gradients in the solution by assuring that flow in the neighborhood of the electrodes was essentially laminar and, if not of short duration, at least uniform.

3.1 Initial Experiments

1) The solution used initially was 0.005 M with respect to $\text{Ce}(\text{HSO}_4)_4$, 0.25 M with respect to NaCl and 0.25 M with respect to H_2SO_4 . When the solution was placed in contact with the mercury pool, the expected conversion of ceric to cerous ion did not take place. An equivalent quantity of $\text{Na}_2\text{C}_2\text{O}_4$ was then added, the products of the reaction being sodium and cerous ions and carbon dioxide.

Investigation of the rectification characteristic was carried out by using the cell as a two electrode device. The expected voltage-current curve was obtained. As long as no extraneous reactions occurred at the electrode, the currents were of the order of microamperes. As the voltage approached within 0.1 v of the apparent decomposition voltage, 1.1 v, the current increased slightly. After attaining the decomposition voltage, the current rapidly increased with incremental increases in applied voltage. These data are shown graphically in Fig. 3. Although the voltage is about that expected for the cerous-ceric conversion, later experiments have shown that the true reaction occurring was the oxidation of chloride ion to chlorine which occurs at nearly the same voltage.

On the basis of the foregoing, the emitter was biased positively and operated in the 1.00 - 1.30 v range. The collector was also biased in the positive direction but was operated from 0.00 - 0.70 v, this region including the flattest portion of the rectification curve.

The data compiled in Table I were obtained with the emitter and collector approximately 0.1 mm apart. After each set of data was taken, the emitter voltage was reduced to the neighborhood of zero and the assembly and the solution allowed to stand after stirring until equilibrium concentrations were reattained. The emitter current is plotted versus the collector current schematically in Fig. 4. The individual datum points indicated are those which are in poorest agreement with the slope of the best line drawn for all of the data. The slope of this curve is $\alpha = (-\partial I_c / \partial I_e) V_c = \text{const}$. Since all of the data fall upon one curve, it is seen that α is essentially independent of the collector voltage in the range studied.

Because the process under investigation is diffusion limited, one would suspect that the modulation as reflected in α is a function of the electrode spacing, d . The parameter d was varied between 0.1 and 1.2 mm. These data are presented graphically in Fig. 5 as emitter current versus collector current plots. It will be noted that α does decrease with increasing d . Figure 6 is a graph of d versus α .

2) A solution was prepared 0.01 M with respect to $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$, 0.25 M with respect to NaCl and 0.1 M with respect to HCl. It was placed over a mercury pool and allowed to come to equilibrium after the spontaneous ferric-ferrous conversion. A rectification curve similar in form to that shown in Fig. 3 was obtained. The flat region of the curve was from 0.20 to 0.70 v. The decomposition voltage was about 1.1 v showing that the reaction again was the chloride-chlorine conversion.

The data obtained in three electrode operation are placed in Table II. The electrode spacing parameter d being of the order of 0.15 mm, the value of α , 0.90, is about that which would be expected on the basis of data obtained in the previous section. Emitter current is plotted against collector current in Fig. 7.

3.2 Chloride-Chlorine Couple

In view of the fact that the rectification curves of the cerous and ferrous ion solutions are nearly the same, although the decomposition voltage of the ferrous ion is about 0.7 v more negative than the former, it was recognized that some other reaction was probably occurring in both. The following experiments showed that the chloride-chlorine reaction was involved.

1) Sulfate Ion Solution

A 0.25 M Na_2SO_4 , 1 M H_2SO_4 solution was prepared. The rectification curve yielded no forward current in the region of 1.1 v. Even at higher potentials, no significant transistor action was obtained. This eliminated the possibility of the anodic oxidation of sulfate ion to persulfate or peroxydisulfate and the reverse.

2) Chloride Ion Solution

A solution 1 M with respect to NaCl and 0.2 M with respect to HCl was prepared. The rectification curve obtained was exactly like those described in Section 3.1. Transistor action was successfully observed with this solution. These data are shown graphically in Fig. 8 and compiled in Table III.

This process is considered to be based upon the chloride-chlorine couple. It is more stable than that attributable to the oxyacids of chlorine except for the chloride-perchlorate couple. The latter couple is eliminated because it is essentially irreversible at low temperatures. Further, one observes the presence of Cl_2 in the solution surrounding the emitter by its typical yellow-green color. The foregoing established the true nature of the experiments carried out earlier as being based upon the oxidation of chloride ion to form chlorine and the reduction of the latter at the collector.

3.3 Ferrous-Ferric Couple

A ferrous ion solution containing 0.25 M FeSO_4 and 1.5 M HCl was investigated. The rectification characteristic curve shown in Fig. 9 indicates the appearance of the expected limiting current. It is evident that the absence of this structure in previous work is attributable to the extremely low concentration of ferrous ion in solution. The electrode separation parameter d being about 0.08 mm, one expects α to be very nearly unity. That this is the case is shown graphically in Fig. 10. The corresponding data are given in Table IV.

The collector current is plotted against the collector voltage for this solution in Fig. 11. The resultant output characteristic indicates that the collector operates independent of its bias in the region from -0.25 v to +0.25 v.

3.4 Bromide-Bromine Couple

It was suggested by Professor H.A. Laitinen that the much more highly reversible bromide-bromine couple might be more satisfactory than the chloride-chlorine couple. This was attempted with the use of two different base electrodes, mercury-mercurous bromide and silver-silver bromide.

1) Mercury-Mercurous Bromide Base Electrode

The rectification characteristic obtained using a solution of 1 M NaBr was identical to that shown in Fig. 3 except for the fact that it was not quite as flat in the low voltage region and the break occurred near 0.8 v.

It is well-known that bromine decomposes water in solutions of low acidity. In the present case, this would result in an increase in α with a decrease in pH. This was investigated in four solutions of pH 7, 4, 2.5 and 1 with the volume and bromide ion concentration remaining constant. Decrease in pH was brought about through the addition of HBr. It was found that the value of α was constant at 0.98. Emitter and collector characteristics for pH 7 and pH 1 are reproduced in Table V.

It is not improbable that in a slightly basic solution this property could be utilized to simulate the phenomenon of recombination of the injected carriers in the base region of a junction transistor.

2) Silver-Silver Bromide Base Electrode

A slight modification of the base electrode contact was made for this experiment. The rectification characteristic using a solution 1 M with respect to NaBr and 0.1 M with respect to HBr was extremely flat from 0.0 to 0.9 v. An unusually high current density was attained as contrasted to other cells used in this research. Although no gas evolution was observed until the applied voltage was in the neighborhood of 2 v, there is a suggestion of an inflection point in the rectification curve at 1.1 v. This, if it is real, would indicate that a process other than the oxidation of bromide to bromine begins at that potential.

In operation as a transistor, this solution yielded $\alpha = 0.92$ with a spacing of about 0.04 mm. This particular solution behaved in exceptional fashion with respect to the output characteristic. These data are presented in Fig. 12.

4. DISCUSSION

The behavior of the electrolytic transistor under the conditions described above is basically as predicted. This extension of the phenomenon of transistor action to the liquid state indicates the generality of the physical analysis of its method of operation.

Two types of electrochemical reactions have been studied. These are the conversion of an ion to an uncharged molecule and the change in valency of an ionic couple. Metal-metal ion couples could be selected in various combinations as could metal-metal salt electrodes in the presence of their anions. The operation of the cell would also be possible with such organic couples as quinone-hydroquinone under various pH conditions. Non-aqueous solvents could also be used.

This model of the electrolytic transistor is limited in current gain to unity in grounded base operation just as is the junction transistor. Since the output impedance is much higher than the input impedance, power gain can be obtained at very low frequencies.

An unexpected result of this investigation was the observation of the fact that the limiting current of several solutions as determined from rectification characteristics was enhanced when the device was placed in three electrode operation. The enhancement was a factor of about two for the chloride-chlorine couple and about eight for the ferrous-ferric couple.

The current is normally limited by diffusion of the majority ion in solution (in these cases the chloride and ferrous ions) to the emitter. The width of the diffusion region is generally determined by convection currents in the liquid. If the spacing between emitter and collector is less than this width, the diffusion path is decreased and the current enhanced. The concentration of the majority ion at the collector is determined by the potential of the collector relative to the solution and is maintained by the reverse reaction which occurs at the collector.

Although the phenomena observed are quite general, it is anticipated that a variety of redox couples and base electrodes will be studied. Plans for the future also include research on the effect of changing the geometry of various components of the cell. For the purpose of perfecting the analogy, the device will be utilized in some simple circuits.

In view of the long time constants of the electrolytic transistor, a further step in this research will be a study of the transient electrical characteristics of the cell. The general pattern of the investigation will involve an essentially discontinuous increase or decrease in the emitter bias with concurrent electro-mechanical recording of the emitter and collector characteristics.

TABLE I

EMITTER AND COLLECTOR CHARACTERISTICS OF THE ELECTROLYTIC TRANSISTOR
(Spacing parameter $d = 0.1$ mm; Cerous-Ceric and Chloride-Chlorine Couples)

I_e (ma)	V_e (v)	I_c (ma)	V_c (v)
0.0735	1.00	- 0.0377	0.70
0.328	1.05	- 0.265	0.70
0.673	1.10	- 0.575	0.70
0.989	1.15	- 0.893	0.70
6.65	1.20	- 6.22	0.70
8.63	1.25	- 8.18	0.70
16.2	1.30	-15.3	0.70
0.084	1.00	- 0.037	0.60
0.325	1.05	- 0.250	0.60
0.655	1.10	- 0.572	0.60
1.008	1.15	- 0.918	0.60
6.33	1.20	- 5.90	0.60
8.23	1.25	- 7.81	0.60
18.5	1.30	-17.7	0.60
0.0618	1.00	- 0.0368	0.50
0.298	1.05	- 0.253	0.50
0.639	1.10	- 0.575	0.50
0.967	1.15	- 0.888	0.50
6.71	1.20	- 6.33	0.50
8.67	1.25	- 8.24	0.50
17.2	1.30	-16.3	0.50
0.0409	1.00	- 0.0565	0.40
0.275	1.05	- 0.262	0.40
0.602	1.10	- 0.563	0.40
0.963	1.15	- 0.908	0.40
6.71	1.20	- 6.33	0.40
8.98	1.25	- 8.55	0.40
18.6	1.30	-17.6	0.40
0.0340	1.00	- 0.0483	0.30
0.303	1.05	- 0.289	0.30
0.613	1.10	- 0.578	0.30
0.951	1.15	- 0.894	0.30
6.73	1.20	- 6.37	0.30
8.93	1.25	- 8.50	0.30
18.7	1.30	-17.8	0.30
0.0333	1.00	- 0.0570	0.20
0.302	1.05	- 0.291	0.20
0.635	1.10	- 0.603	0.20
1.004	1.15	- 0.954	0.20
6.96	1.20	- 6.55	0.20
9.17	1.25	- 8.74	0.20
20.7	1.30	-19.8	0.20

TABLE I (Cont.)			
I_e (ma)	V_e (v)	I_c (ma)	V_c (v)
0.03	1.00	- 0.09	0.10
0.261	1.05	- 0.281	0.10
0.642	1.10	- 0.625	0.10
1.006	1.15	- 0.976	0.10
6.79	1.20	- 6.42	0.10
9.20	1.25	- 8.81	0.10
20.7	1.30	-19.7	0.10
0.0753	1.00	- 0.0533	0.00
0.320	1.05	- 0.267	0.00
0.675	1.10	- 0.600	0.00
4.56	1.15	- 4.22	0.00
6.83	1.20	- 6.49	0.00
8.45	1.25	- 8.10	0.00
14.0	1.30	-13.7	0.00

TABLE II
 EMITTER AND COLLECTOR CHARACTERISTICS OF THE ELECTROLYTIC TRANSISTOR
 (Spacing parameter $d = 0.15$ mm; Ferrous-Ferric and Chloride-Chlorine Couples)

I_e (ma)	V_e (v)	I_c (ma)	V_c (v)
0.252	1.00	- 0.273	0.30
0.641	1.10	- 0.589	0.30
4.16	1.20	- 3.71	0.30
6.67	1.30	- 5.98	0.30
0.237	1.00	- 0.218	0.40
0.707	1.10	- 0.630	0.40
4.39	1.20	- 3.96	0.40
6.83	1.30	- 6.29	0.40
0.082	1.00	- 0.074	0.50
0.546	1.10	- 0.451	0.50
3.97	1.20	- 3.46	0.50
6.71	1.30	- 6.14	0.50

TABLE III
 EMITTER AND COLLECTOR CHARACTERISTICS OF THE ELECTROLYTIC TRANSISTOR
 (Chloride-Chlorine Couple)

I_e (ma)	V_e (v)	I_c (ma)	V_c (v)
0.154	1.00	- 0.123	0.00
0.482	1.05	- 0.418	0.00
2.42	1.10	- 2.17	0.00
5.17	1.15	- 4.80	0.00
7.32	1.18	- 6.89	0.00
9.09	1.23	- 8.62	0.00
0.0467	1.00	- 0.0836	0.30
0.389	1.05	- 0.337	0.30
2.21	1.10	- 1.97	0.30
5.33	1.15	- 5.02	0.30
7.43	1.20	- 7.03	0.30
8.64	1.25	- 8.23	0.30

TABLE IV
EMITTER AND COLLECTOR CHARACTERISTICS OF THE ELECTROLYTIC TRANSISTOR
(Spacing parameter $d = 0.08$ mm; Ferrous-Ferric Couple)

I_e (ma)	V_e (v)	I_c (ma)	V_c (v)
1.30	0.32	- 1.37	0.00
4.05	0.40	- 4.00	0.00
8.25	0.43	- 8.12	0.00
10.0	0.44	- 9.86	0.00
15.2	0.46	-15.5	0.00
20.8	0.50	-21.0	0.00
30.6	0.57	-30.3	0.00

TABLE V
EMITTER AND COLLECTOR CHARACTERISTICS OF BROMIDE-BROMINE COUPLE AS A FUNCTION OF pH
(Spacing parameter $d = 0.03$ mm)

	I_e (ma)	V_e (v)	I_c (ma)	V_c (v)
pH 7	0.506	0.89	- 0.480	0.25
	1.41	0.91	- 1.32	0.25
	2.67	0.93	- 2.57	0.25
	5.16	0.96	- 5.05	0.25
	7.63	0.98	- 7.52	0.25
	9.62	1.00	- 9.50	0.25
pH 1	0.376	0.89	- 0.363	0.25
	0.951	0.92	- 0.920	0.25
	2.24	0.92	- 2.12	0.25
	4.84	0.95	- 4.67	0.25
	6.87	0.97	- 6.70	0.25
	9.33	0.99	- 9.10	0.25

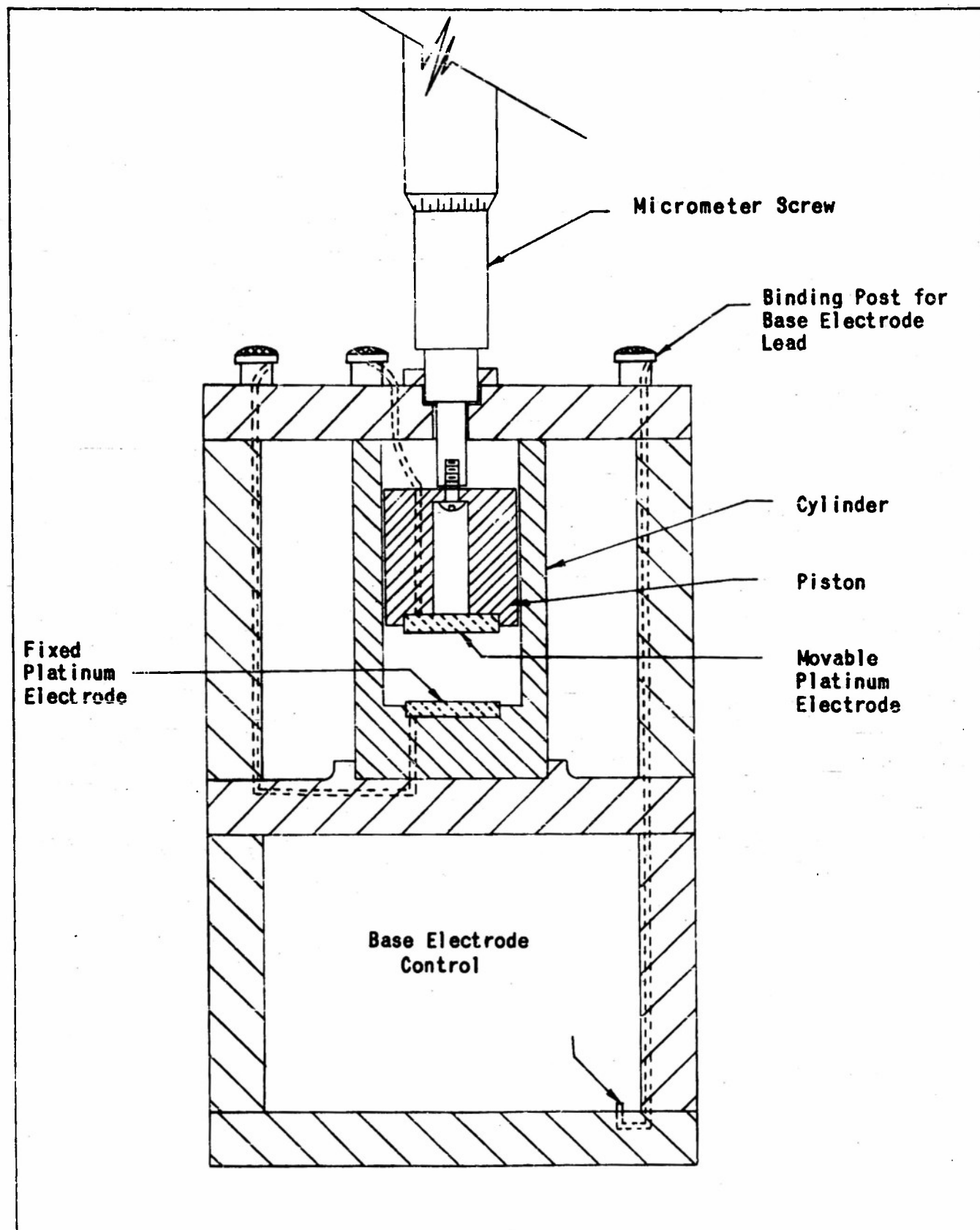


FIGURE 1. VARIABLE SPACED ELECTROLYTIC ANALOGUE TRANSISTOR CELL.

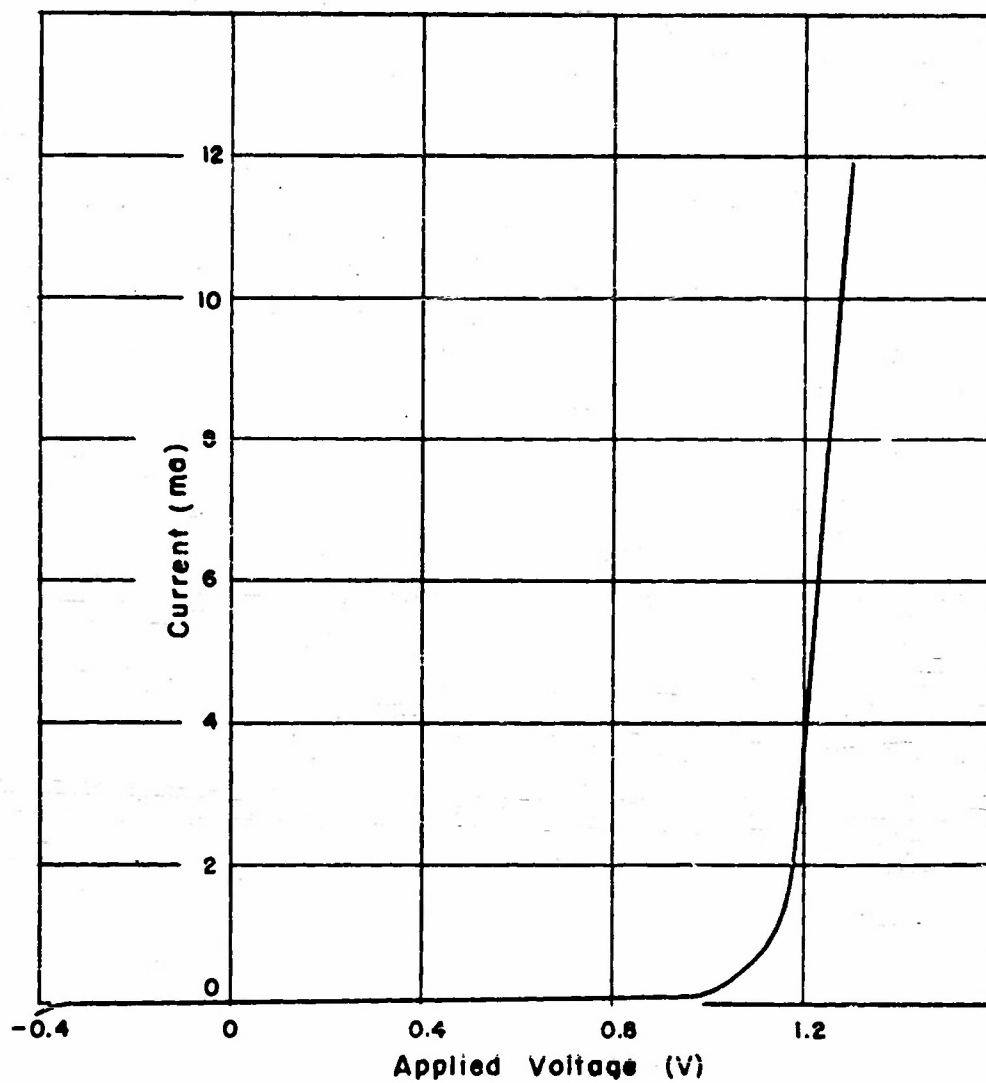


FIGURE 3. RECTIFICATION CHARACTERISTIC FOR THE CHLORIDE-CHLORINE COUPLE.

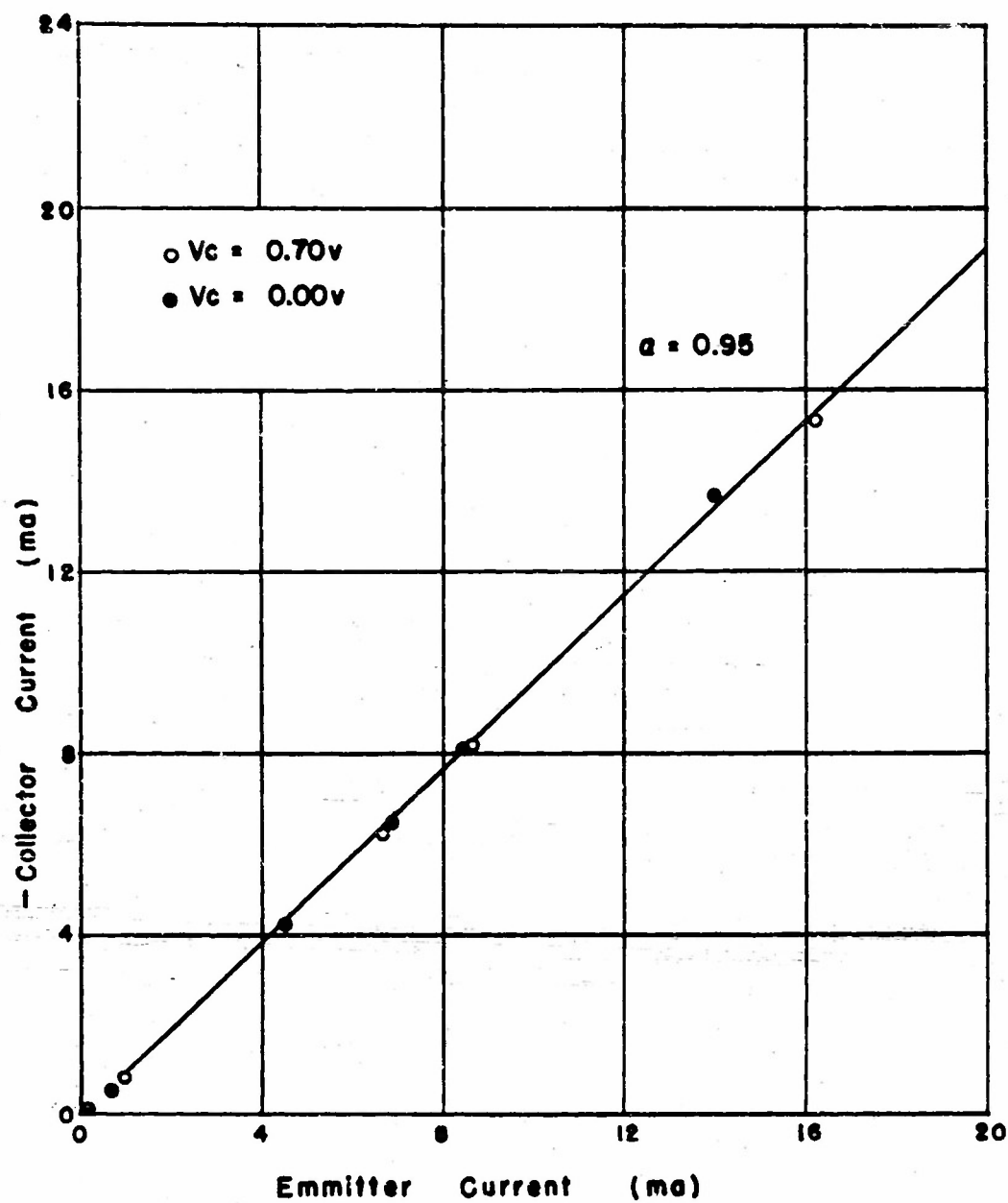


FIGURE 4. ELECTROLYTIC TRANSISTOR CURRENT CHARACTERISTICS
FOR THE CHLORIDE-CHLORINE COUPLE

- $d = 0.1$ mm.
- $d = 0.2$ mm.
- $d = 0.4$ mm.
- $d = 0.8$ mm.
- $d = 1.2$ mm.

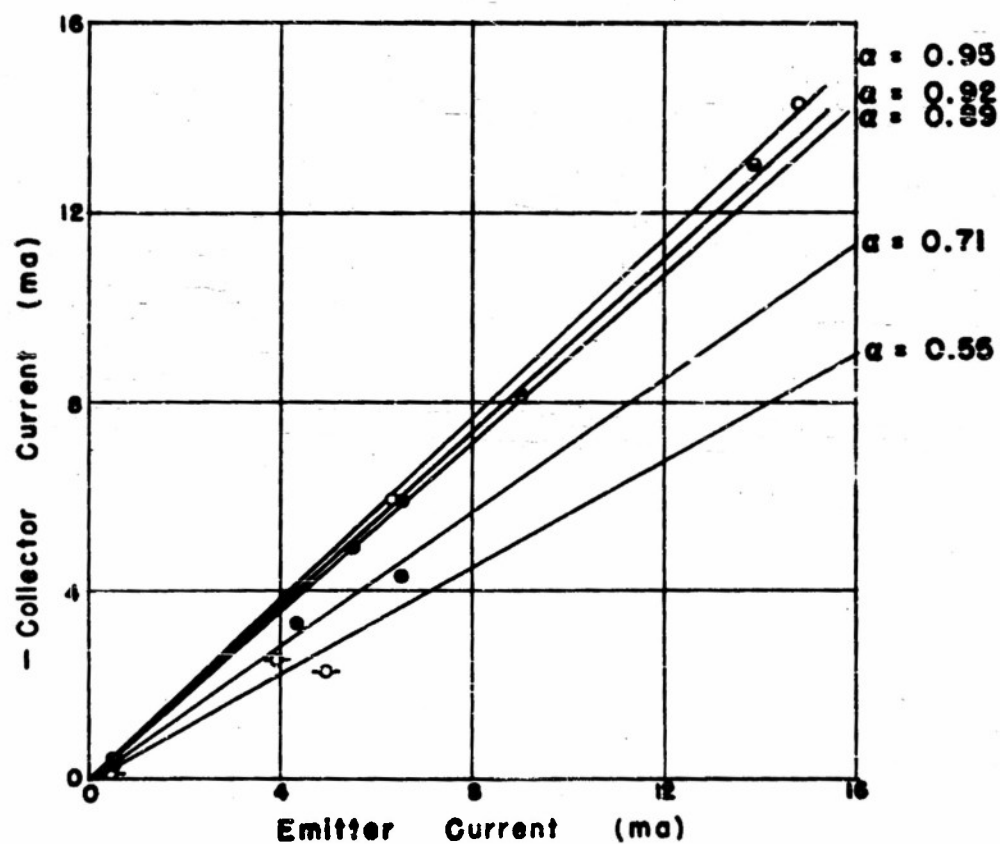


FIGURE 5. ELECTROLYTIC TRANSISTOR CURRENT CHARACTERISTICS FOR THE CHLORIDE-CHLORINE COUPLE AS A FUNCTION OF EMITTER-COLLECTOR SPACING.

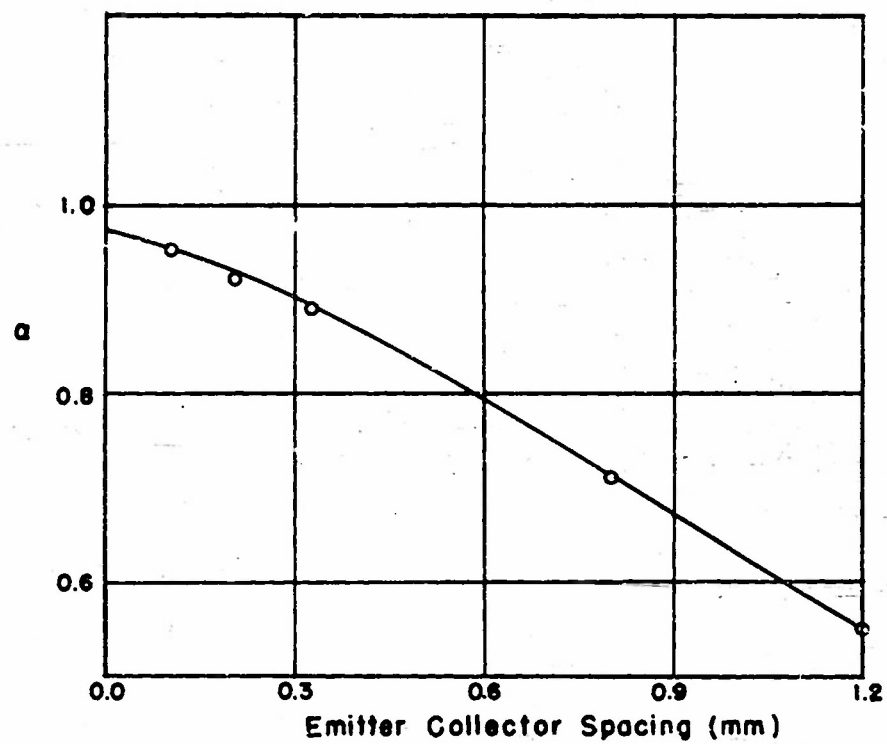


FIGURE 6. α AS A FUNCTION OF EMITTER-COLLECTOR SPACING FOR THE CHLORIDE-CHLORINE COUPLE.

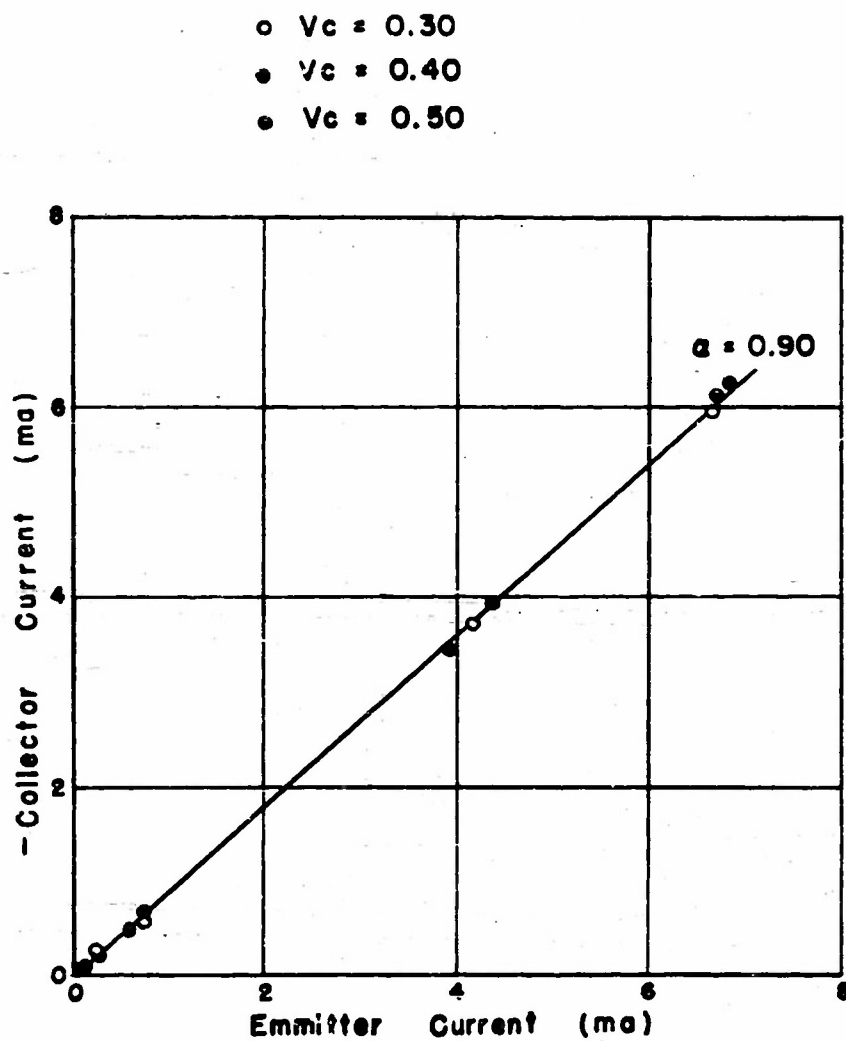


FIGURE 7. ELECTROLYTIC TRANSISTOR CURRENT CHARACTERISTICS FOR THE CHLORIDE-CHLORINE COUPLE.

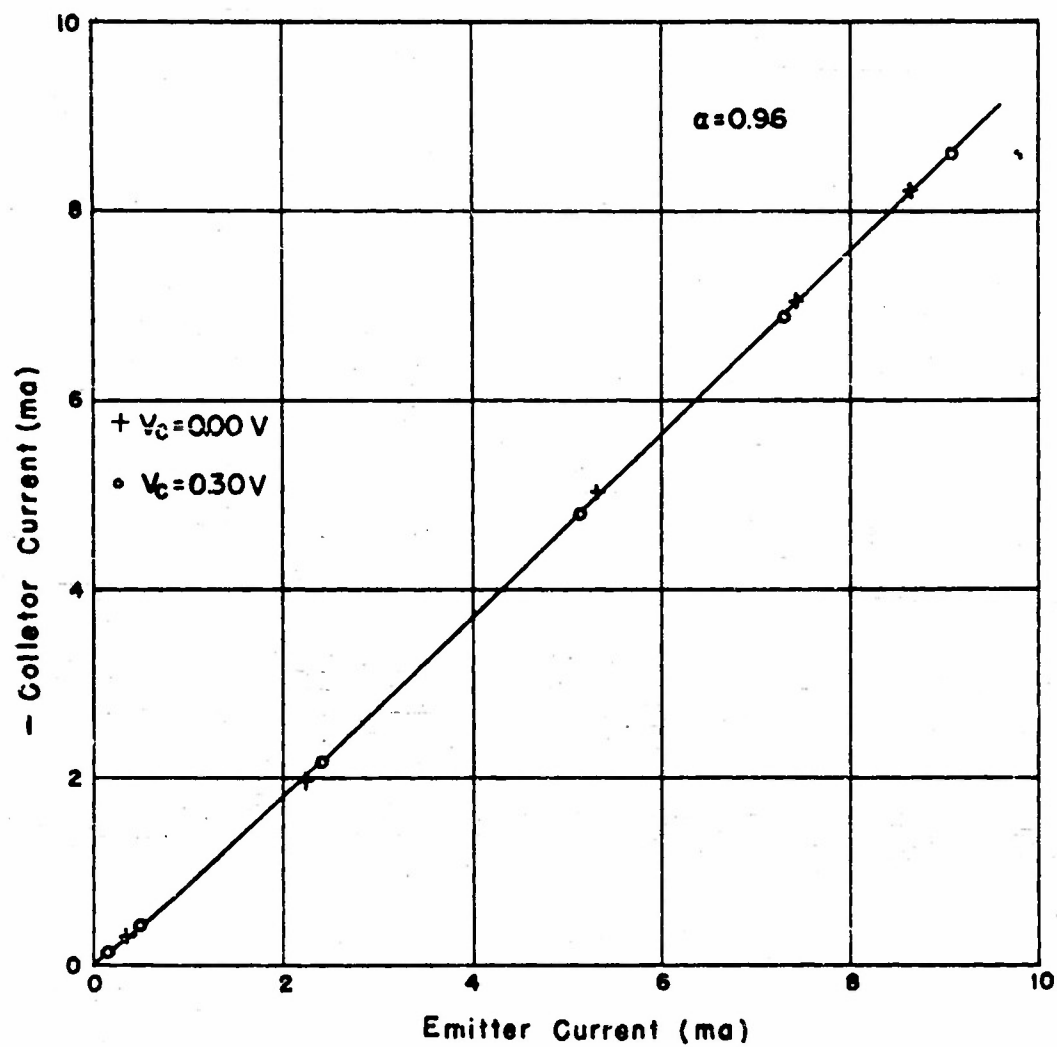


FIGURE 8. ELECTROLYTIC TRANSISTOR CURRENT CHARACTERISTICS FOR THE CHLORIDE-CHLORINE COUPLE.

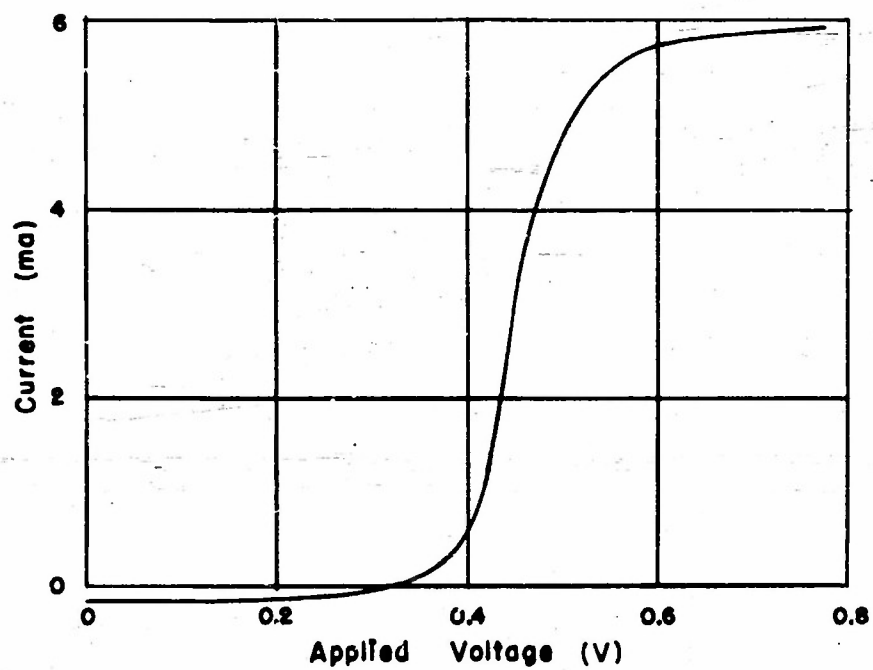


FIGURE 9. RECTIFICATION CHARACTERISTIC
FOR THE FERROUS-FERRIC COUPLE

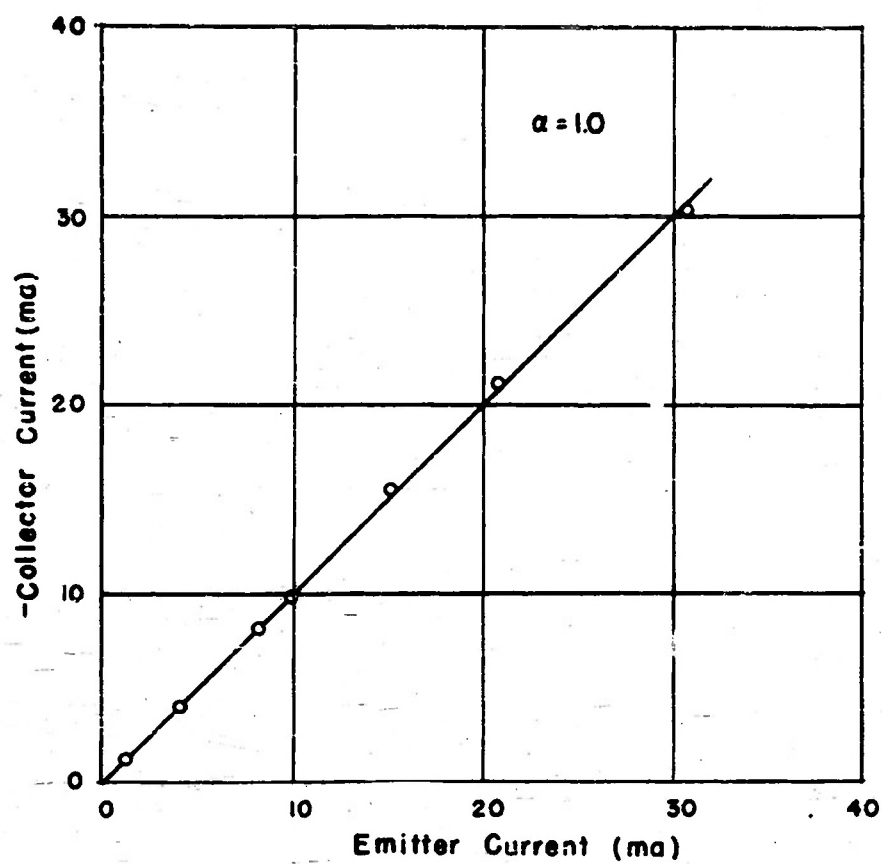


FIGURE 10 ELECTROLYTIC TRANSISTOR CURRENT CHARACTERISTIC FOR THE FERROUS-FERRIC COUPLE

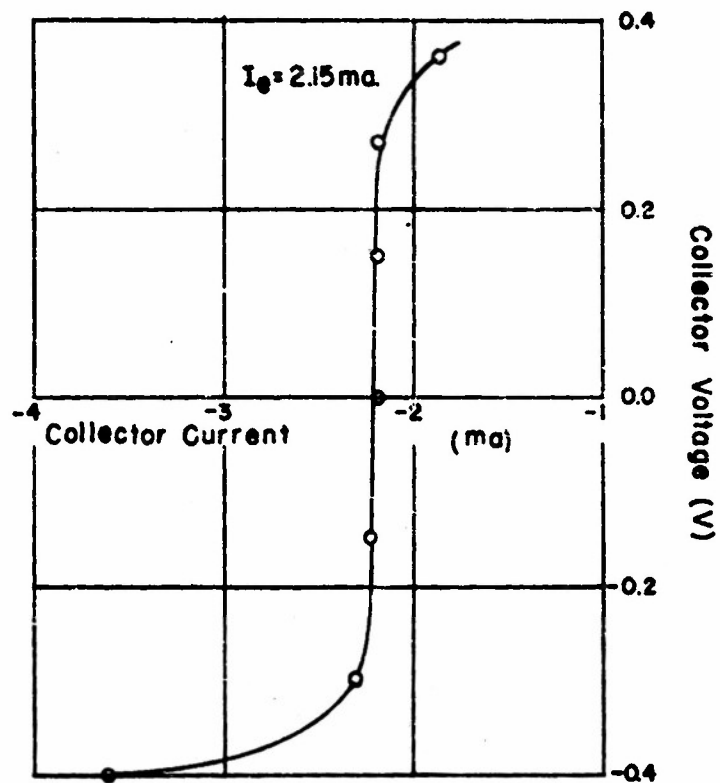


FIGURE 11. ELECTROLYTIC TRANSISTOR OUTPUT CHARACTERISTIC FOR THE FERROUS-FERRIC COUPLE.

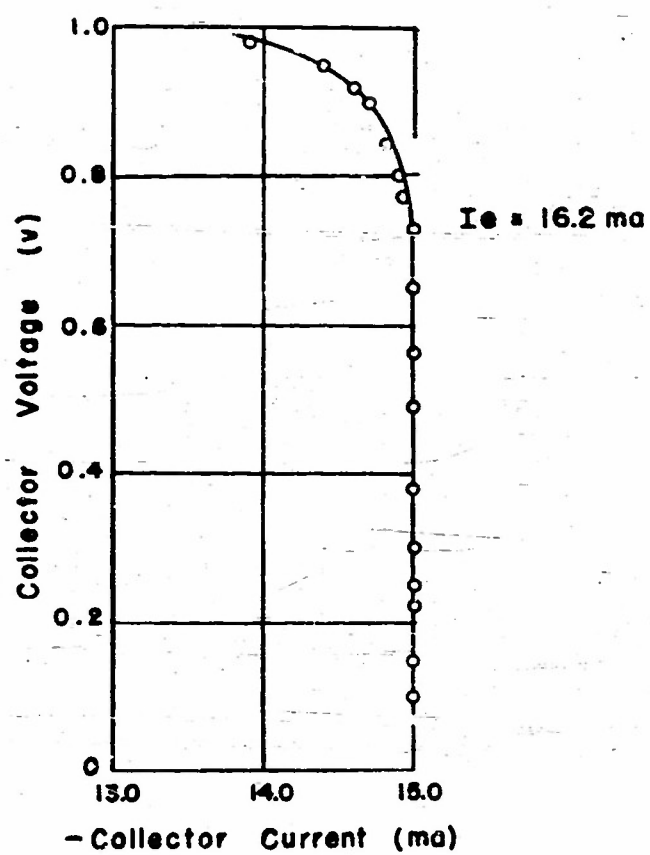


FIGURE 12. ELECTROLYTIC TRANSISTOR OUTPUT CHARACTERISTIC FOR THE BROMIDE-BROMINE COUPLE AND SILVER-SILVER BROMIDE BASE ELECTRODE.