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ELECTRODE PASSIVATION STUDIES

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ABSTRACT

Studies of the passivation of Zn-Fe, Zn-Mn, Zn-Co, and Zn-Ni alloys were made potentiostatically. Alloys of 90 Zn - 10 Fe corrode at a high rate even when passive. Alloys of 83 Zn - 17 Mn have low, active dissolution currents. The 89 Zn - 11 Co alloys have high dissolution currents in the passive state, while the 78 Zn - 22 Co and 80 Zn - 20 Ni alloys appear promising as anodes which may be kept in a passive, reserve state. These two alloys have acceptably high critical currents and low passive currents. Their activation characteristics were studied in detail in 6N KOH; activation to about 75% of the original current density can be achieved in 20 to 90 sec, depending on the alloy and its history.

Studies of Cr, Al, and of amalgams of Mg show them to be unsuitable for use as reserve anodes.

Initial studies of the passivation of Zn-Co and Zn-Ni in electrolytes containing sulfate and chloride ions showed that their dissolution behavior is similar to that in KOH alone.

I. INTRODUCTION

During this quarter we concentrated our studies on zinc alloys. We examined Zn-Fe, Zn-Mn, Zn-Co, and Zn-Ni alloys with particular emphasis on the last two. The active dissolution, passivation, and reactivation of passivated zinc-alloy anodes were investigated in alkaline solution varying in concentration from 1 to 6N in KOH. The 1N alkali is less aggressive than the normal battery electrolyte and can be used to establish whether a given system has sufficient promise to merit further investigation. The 6N KOH simulates closely battery electrolytes currently in use.

The activation characteristics of promising alloys were examined in some detail. The passive layer of the Zn-Ni alloy is difficult to reduce even at fairly negative potentials. However, films formed at high positive potentials can be reduced with greater ease. A series of experiments was carried out in which the passive layer was first pretreated at an anodic potential and then the electrode activated at 0.0 v. It was observed that anodic pretreatment leads to faster activation. The Zn-Co alloys are generally activated with less difficulty than the corresponding Zn-Ni alloys.

The zinc-cobalt and zinc-nickel systems were studied in electrolytes N in KOH with additions of various salts. Electrolytes examined so far include $\text{SO}_4^{=}$ and Cl^- . The data are not complete as yet, but it appears that, in general, the behavior of these alloys is approximately the same in N KOH and in N KOH containing the above salts. However, small changes of the passive current and of the critical current and some differences in the time dependence of the passive current were observed in solutions containing neutral salts.

II. WORK COMPLETED UNDER CONTRACT

A. Zinc Alloys

1. Selection of Alloys

The factors governing the choice of alloying elements were discussed in the last quarterly report. Of the elements judged to be promising, alloys of Zn with Cu and Mg have been examined with the results reported⁽¹⁾. During the current period Zn-Fe, Zn-Mn, Zn-Co, and Zn-Ni alloys were studied.

2. Experimental

a. Alloys

The desired composition of the Zn-Co alloys is within the γ -phase of the Zn-Co system (between 76-86 wt % Zn). Alloys which we have made varied somewhat in composition; most of the work was done with an alloy having a composition of 78 Zn - 22 Co, as determined by chemical analysis. Metallographic examination of the alloys showed them to be single phase, with some voids present at grain boundaries. It is not unusual for voids to appear in the grain boundaries during solidification of intermetallic compounds.

Zn-Ni alloys were prepared with a composition, as determined by chemical analysis, of 79.2 Zn and 20.3 Ni. The material was examined by obtaining an X-ray powder pattern and found to be single phase. Its structure conformed to that of NiZn_3 . An X-ray line which could not be identified was not due to either free Zn or free Ni.

b. Electrochemical Measurements

The experimental arrangement for the study of current-potential curves was described in the last quarterly report. Briefly, this involves a three-compartment, Pyrex cell using a hydrogen electrode as reference. The working electrode is usually a polished cylinder which is tapped, threaded, and mounted on a Teflon gasket.

Most of the experimental work was done in the absence of stirring in KOH containing no zincate since these conditions best simulate the conditions in a primary battery. Where appropriate, the potential was stepped by an electronic potentiostat so as to evolve hydrogen in between each point on the anodic, polarization curve. This treatment tends to dissolve passive films which may be formed at positive potentials.

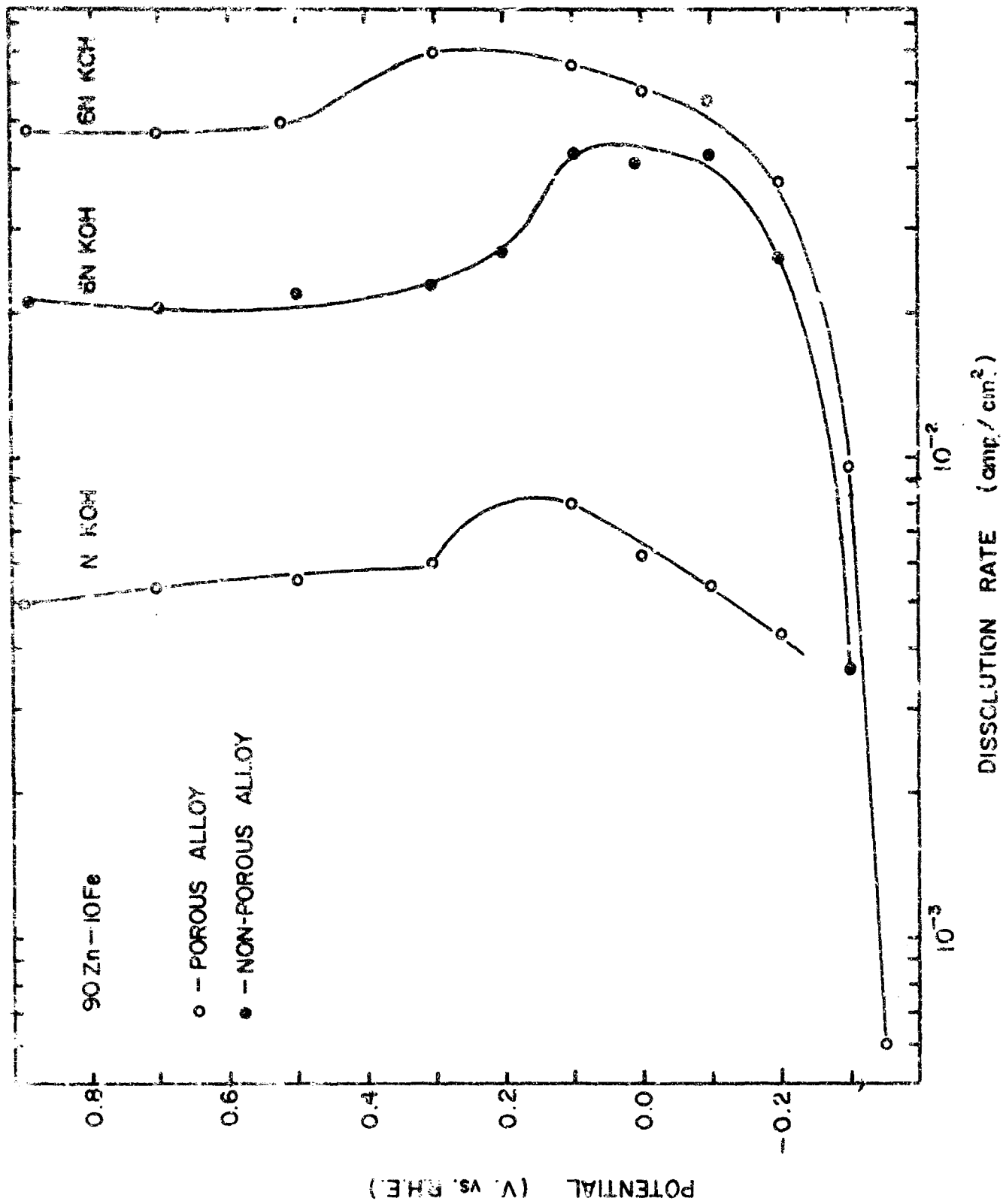
At each potential of interest, we record the current as a function of time and observe any changes in the appearance of the electrode. When the current is steady (generally 5 min), we revert to hydrogen evolution and then to the next positive potential. In this way, we can reproduce currents in the course of an extended experiment, or from sample to sample, to within 10%.

3. Zinc-Iron Anodes

Typical current-potential curves for an alloy with a nominal composition of 90 Zn - 10 Fe are shown in Fig. 1. (The precise composition of the alloy will be determined by chemical analysis.) Considerable difficulty was experienced in obtaining alloys free of pores or voids. The difference in behavior between nonporous alloys and alloys containing voids is shown in the figure and is essentially what is expected from differences in surface area.

The curves show an active-passive behavior, but the current in the passive range is substantial (about 20 ma/cm^2 in 6N KOH for a nonporous alloy). The high passive current is somewhat surprising in view of the stability of passive films on iron in alkaline solutions. It appears that approximately 10% of Fe lowers but slightly the passive current (compare to 50 ma/cm^2 for pure Zn in 6N KOH). The critical current is also lowered by addition of iron from about 300 ma/cm^2 for pure zinc to about 40 ma/cm^2 for the 90 Zn - 10 Fe alloy; the current potential curve in the active region is also generally shifted to more positive potentials.

Fig. 1 Anodic Dissolution of 90 Zn - 10 Fe Alloy at 33°C, unstirred



It appears from the above that addition of 10% Fe improves the passive behavior little while it makes the active dissolution characteristics significantly less desirable than those of pure zinc. It is not clear at the moment whether similar effects will be observed at higher iron contents (20% and 30% Fe).

4. Zinc-Manganese Alloys

As mentioned previously, Mn appears sufficiently corrosion resistant to KOH to be used as a possible alloying addition for improving the passive behavior of Zn. Results for a nominal composition of 83 Zn - 17 Mn in N KOH are shown in Fig. 2 which gives currents taken at 5 min at each potential with a progression up the curve in the usual point-by-point fashion. The currents were fairly steady ($< 10\%$ change in 3 to 5 min). The open-circuit potential was -0.30 v vs RHE, a little more positive than Zn itself, and the maximum active dissolution current (~ 3 mA/cm²) was found at quite low potentials (~ -0.25 v). Both of these are desirable if we are to maintain the power density of the battery system. However, even at this potential the electrode turned black and at higher potentials a long, gradual passivation was observed. The minimum current (~ 0.6 mA/cm²) was too high for the present purpose and also occurred at too high a potential (~ 1.3 v vs RHE, which is too close to the Ag/AgO potential). Although the general character of the corrosion of the Zn-Mn alloy is qualitatively suitable for our purpose, the corrosion rate is too high in the passive region and too low in the active region. Consequently, the material was not tested in 6N KOH.

5. Zinc-Cobalt Alloys

We indicated previously that Co showed some promise as an alloying constituent, and consequently, we have examined the behavior of 78 Zn - 22 Co. The current-potential curve for this alloy in 1N KOH is shown in Fig. 3. The rest potential was about -0.15 v vs RHE, somewhat higher than Zn, but the active

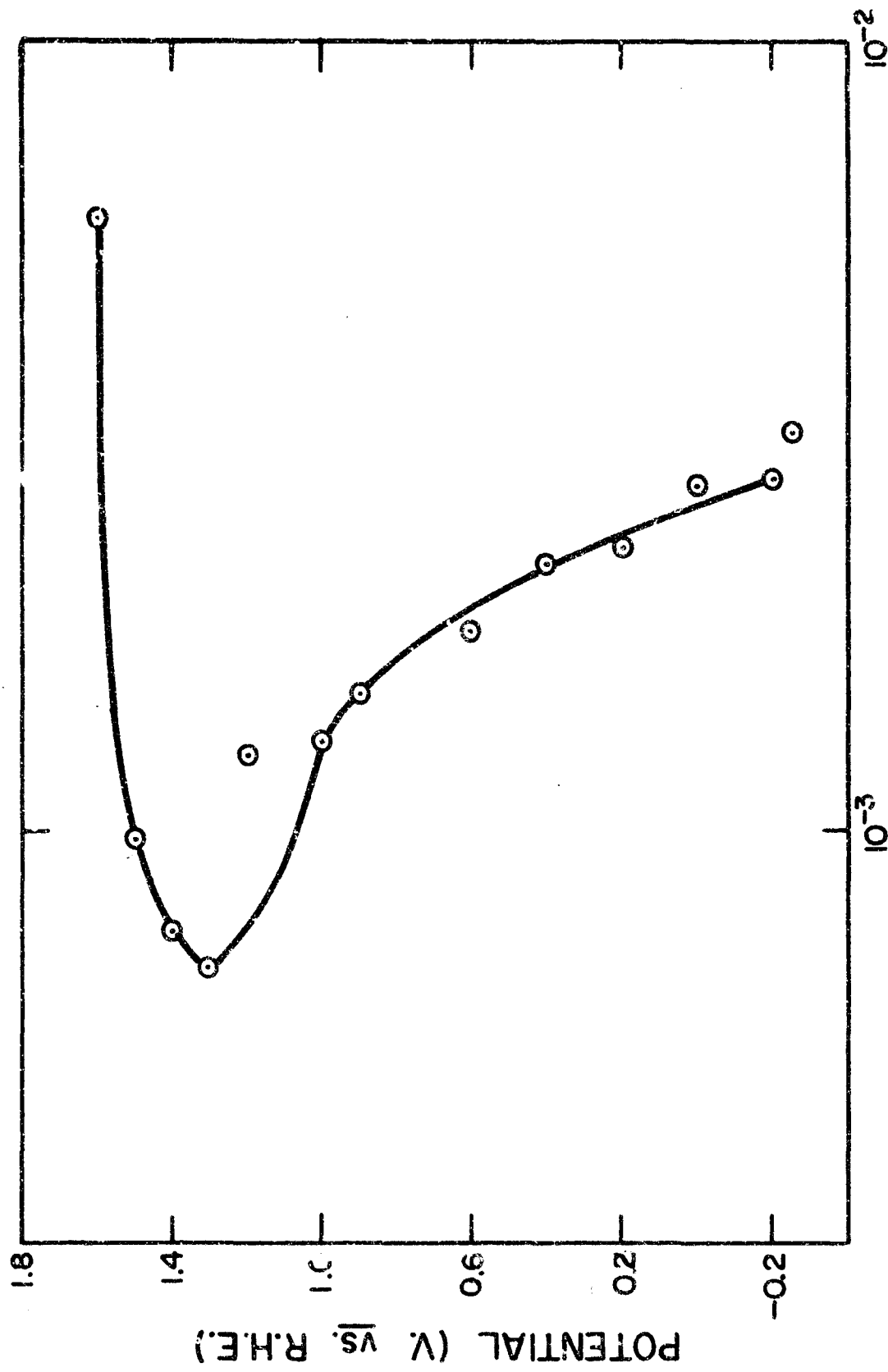


Fig. 2 Anodic Dissolution of 83 Zn - 17 Mn in 1 N KOH at 30°C, unstirred.

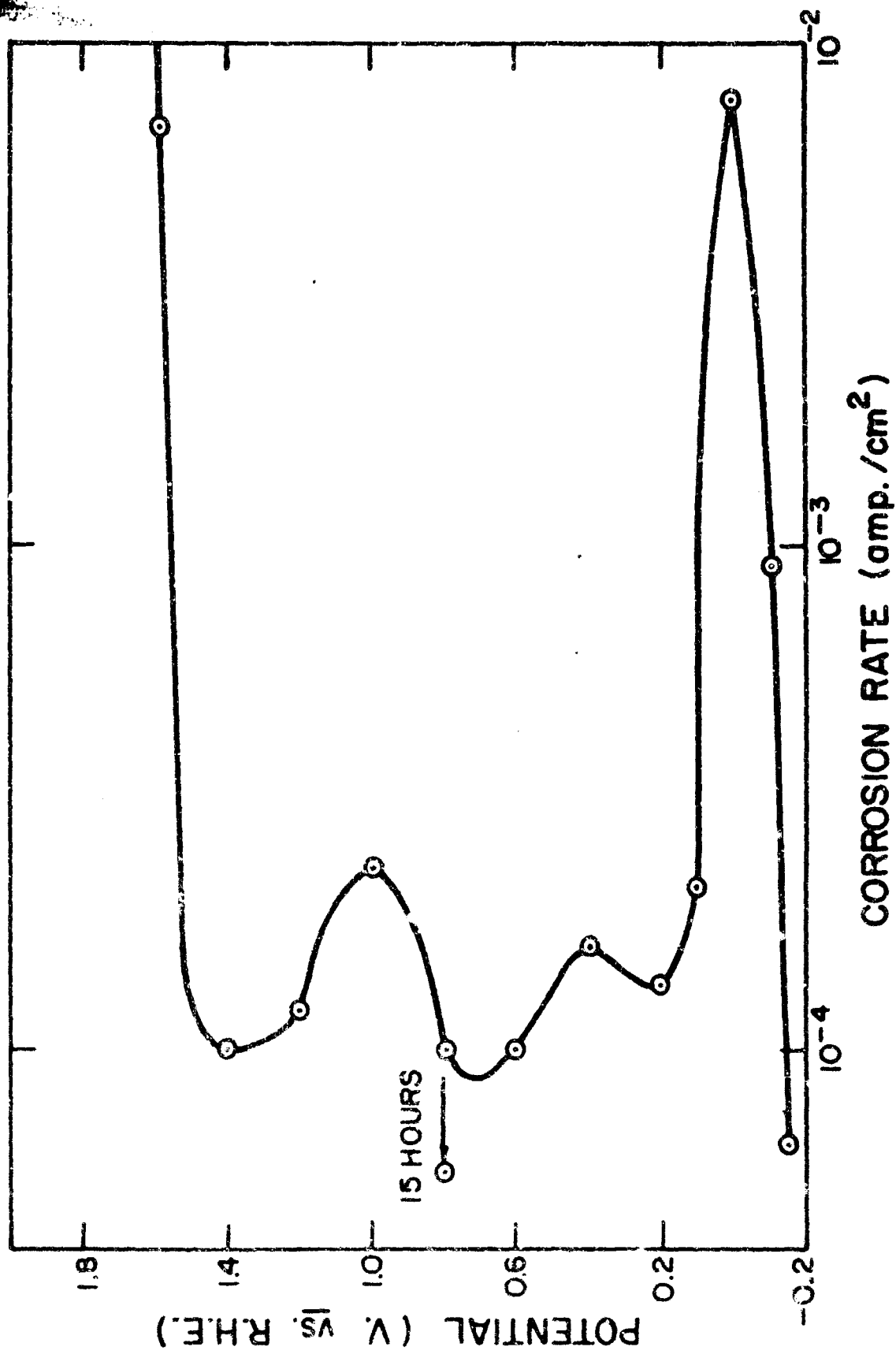


Fig. 3 Anodic Dissolution of 81 Zn - 19 Co in 1 N KOH at 30°C, unstirred.

dissolution occurred at a reasonably low potential. Thus the critical current of $\sim 7.5 \text{ mA/cm}^2$ was found at $\sim 0.0 \text{ v vs RHE}$.

Below this potential some H_2 -evolution was observed. This means that the actual corrosion rates in this region are higher than those shown in Fig. 3. A separate experiment on a fresh sample which had not been passivated showed that H_2 -evolution at open circuit (-0.15 v) is about $300 \mu\text{A/cm}^2$, and while this undoubtedly varies with the state of the surface, it does not cause a serious error in the data of Fig. 3.

The current-potential curve of Fig. 3 is most promising: the critical current is reasonably high and the passive current is interestingly low ($\sim 150 \mu\text{A/cm}^2$) and observed over a wide range of potential (0.2 to $\sim 1.5 \text{ v}$). After 15 hours at 0.8 v , the passive current fell to $55 \mu\text{A/cm}^2$. For Zn itself in 1N KOH , i_c is $\sim 35 \text{ mA/cm}^2$ and i_p is $\sim 4.5 \text{ mA/cm}^2$. The ratios of the critical currents (the maximum current we can draw from the anode) in going from Zn to the alloy is ~ 0.22 , while the ratio of passive currents is ~ 0.012 . Thus, we have only depressed i_c by a factor of 5 but we have lowered i_p by about 80 times. The Co-Zn system is evidently approaching the desired behavior for a passive-reserve battery, although its passive current is still too high.

After 15 hours at 0.8 v , the electrode was black and difficult to activate. After 64 hours at 0.2 v , the electrode was black and shiny and the passive current was $56 \mu\text{A/cm}^2$. H_2 -evolution occurred on this black layer when a cathodic pulse was applied, and complete activation of the electrode with cathodic pulses did not appear possible. Thus at 0.0 v , the current was only $\sim 1.3 \text{ mA/cm}^2$ (as against $\sim 7.5 \text{ mA/cm}^2$ for the original specimen).

In 6N KOH , the $78 \text{ Zn} - 22 \text{ Co}$ alloy also showed promising behavior (Fig. 4). The rest potential was -0.16 v and a separate experiment showed that H_2 -evolution at open circuit was 1.0 mA/cm^2 . The current in the active dissolution region ($< 0.0 \text{ v}$) was quite

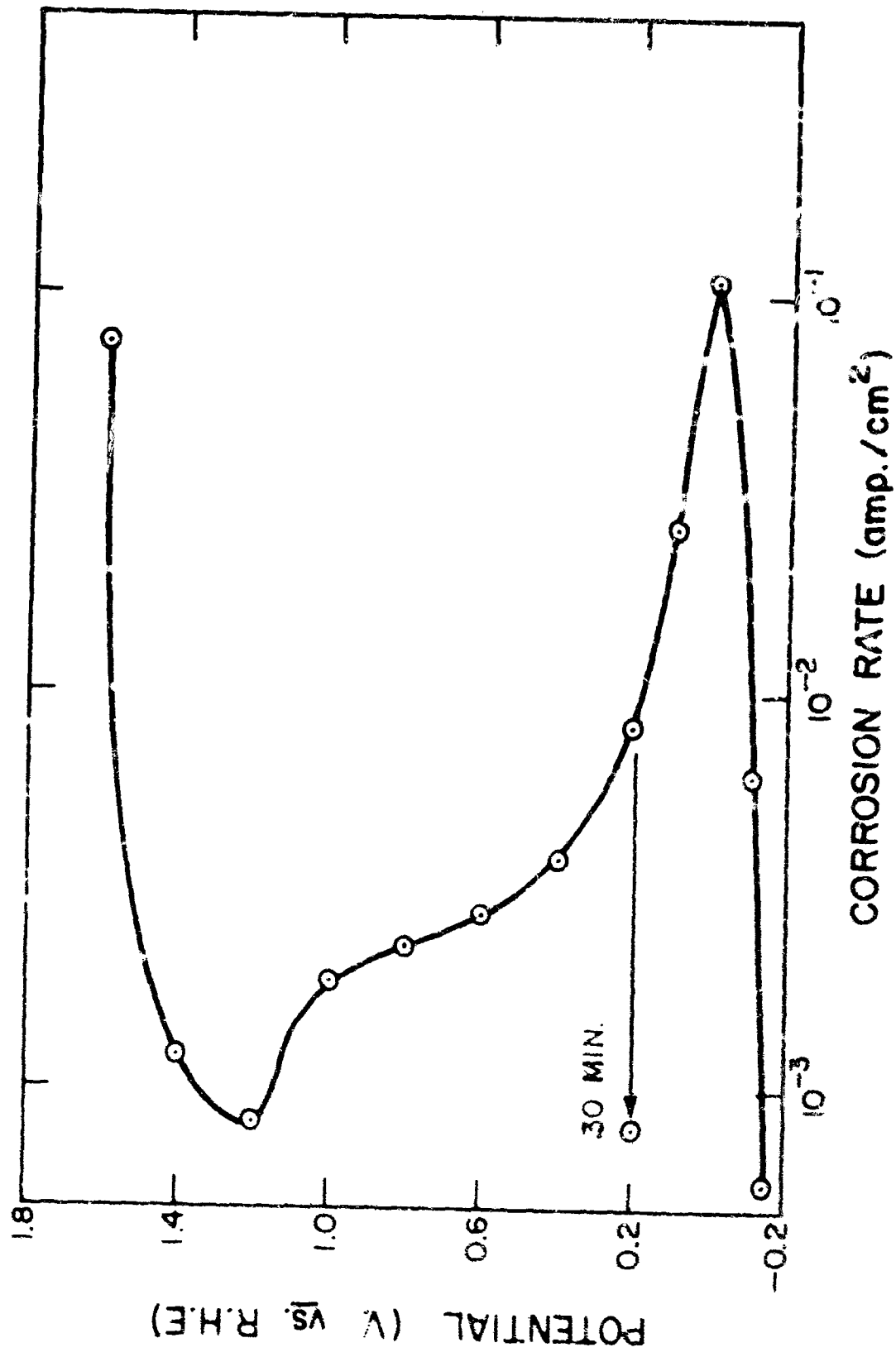


Fig. 4 Anodic Dissolution of 78 Zn - 22 Co in 6 N KOH at 30°C, unstirred.

steady but above this, fell with time. The data in Fig. 4 are for currents taken point-by-point after 5 min at each potential. At 0.1 v the electrode became black and remained so subsequently. The critical current is 110 mA/cm^2 (vs. 350 mA/cm^2 for Zn, a ratio of 0.31), and the passive current (after 15 hours at 0.2 v) is 0.21 mA/cm^2 (vs. 55 mA/cm^2 for Zn, a ratio of 0.004). Thus the alloy is much better than Zn and better, relatively, than in 1N KOH. The passive current is now, of course, too large ($210 \text{ } \mu\text{A/cm}^2$) for use in the passive reserve mode.

Galvanostatic activation was attempted after potentiostating in the passive region (+0.2 v). After 30 min at 0.2 v, a black layer formed on the electrode which was partially reduced during a -150 mA/cm^2 charging current. The remainder peeled off when H_2 -evolution was reached. The current at 0.0 v was 63 mA/cm^2 as against the original 110 mA/cm^2 . Subsequent alternate treatments of +0.2 v and -150 mA/cm^2 led to further deactivation, viz. currents of 33 and 9 mA/cm^2 . Attempted activation after 15 hours at 0.20 v (during which the current went down to $210 \text{ } \mu\text{A/cm}^2$) was quite successful, viz. 1.5 coul/cm^2 at -300 mA/cm^2 yields a current of 20 mA/cm^2 at 0.0 v. A further 3 coul/cm^2 activated the electrode to 29 mA/cm^2 . These results are summarized in Table I.

Thus, the 78 Zn - 22 Co alloy is reasonably promising in KOH solutions in that its passive current is approaching the desired level, its i_c/i_p ratio ($\sim 500:1$ in 6N KOH) is also approaching an acceptable level, and it can be activated to a considerable extent, at least in 6N KOH. The passive current is probably controlled by the solubility of the appropriate passivating film and it may be possible to limit this by additions to the electrolyte.

An alloy containing less cobalt was also studied. This had a nominal composition of 89 Zn - 11 Co, which corresponds to the γ_1 phase of the Zn-Co system. Polarization curves for this alloy are shown in Fig. 5.

Table I

Activation of 77.8 Zn - 21.6 Co Alloy
6N KOH at 30.0°C in N₂-Saturated Solutions

I.	<u>Passive Potential</u>	<u>Current (ma/cm²)</u>			
		<u>1 min</u>	<u>3 min</u>	<u>5 min</u>	
	+ 0.20 v	+ 30	9.6	7.5	
Activate by 300 ma/cm ² cathodic pulse for 20 sec.					
		<u>10 sec</u>	<u>30 sec</u>	<u>60 sec</u>	<u>120 sec</u>
	Current at 0.0 v	2.7 ma/cm ²	1.1	1.1	2.1
	% Activation	29%	14.5	14.5	27

II.	<u>Passive Potential</u>	<u>Current (ma/cm²)</u>			
		<u>30 min</u>			
	+ 0.20 v	1.4 ma/cm ²			
Activate by 300 ma/cm ² cathodic pulse for 30 sec.					
		<u>10 sec</u>	<u>30 sec</u>	<u>60 sec</u>	<u>120 sec</u>
	Current at 0.0 v	48 ma/cm ²	54	72	69
	% Activation	50%	56	75	72

Table I (Cont.)

III. <u>Passive Potential</u>	<u>Current (ma/cm²)</u>			
	<u>30 min</u>			
	+ 0.20 v 1.1 ma/cm ²			
	Activate at - 0.3 v (~ 360 ma/cm ² cathodic) for 30 sec.			
	<u>10 sec</u>	<u>30 sec</u>	<u>60 sec</u>	<u>120 sec</u>
Current at 0.0v	78 ma/cm ²	72	75	75
% Activation	75%	65	68	68

IV. <u>Passive Potential</u>	<u>Current (ma/cm²)</u>			
	<u>30 min</u>			
	+ 0.2 v 1.4			
	Activate at - 0.25 v (~ 210 ma/cm ² cathodic) for 30 sec.			
	<u>10 sec</u>	<u>30 sec</u>	<u>60 sec</u>	<u>120 sec</u>
Current at 0.0 v	45 ma/cm ²	42	57	60
% Activation	45%	42	57	60

V. <u>Passive Potential</u>	<u>Current (ma/cm²)</u>			
	<u>15 min</u>			
	+ 0.2 v 1.4			
	+ 0.8 v 2.6			
	+ 1.2 v 1.2			
	Activate at - 0.3 v (~ 300 ma/cm ² cathodic) for 30 sec.			
	10 sec	30 sec	60 sec	120 sec
Current at 0.0v	54 ma/cm ²	48	48	54
% Activation	52%	46	46	52

Table I (Cont.)

VI. <u>Passive Potential</u>	<u>Current (ma/cm²)</u>			
	<u>30 min</u>			
+0.2 v	1.4 m			
Activate at - 0.3 v (~ 420 ma/cm ² cathodic) for 30 sec.				
	<u>10 sec</u>	<u>30 sec</u>	<u>60 sec</u>	<u>120 sec</u>
Current at 0.0 v	75 ma/cm ²	69	69	75
% Activation	66%	61	61	66

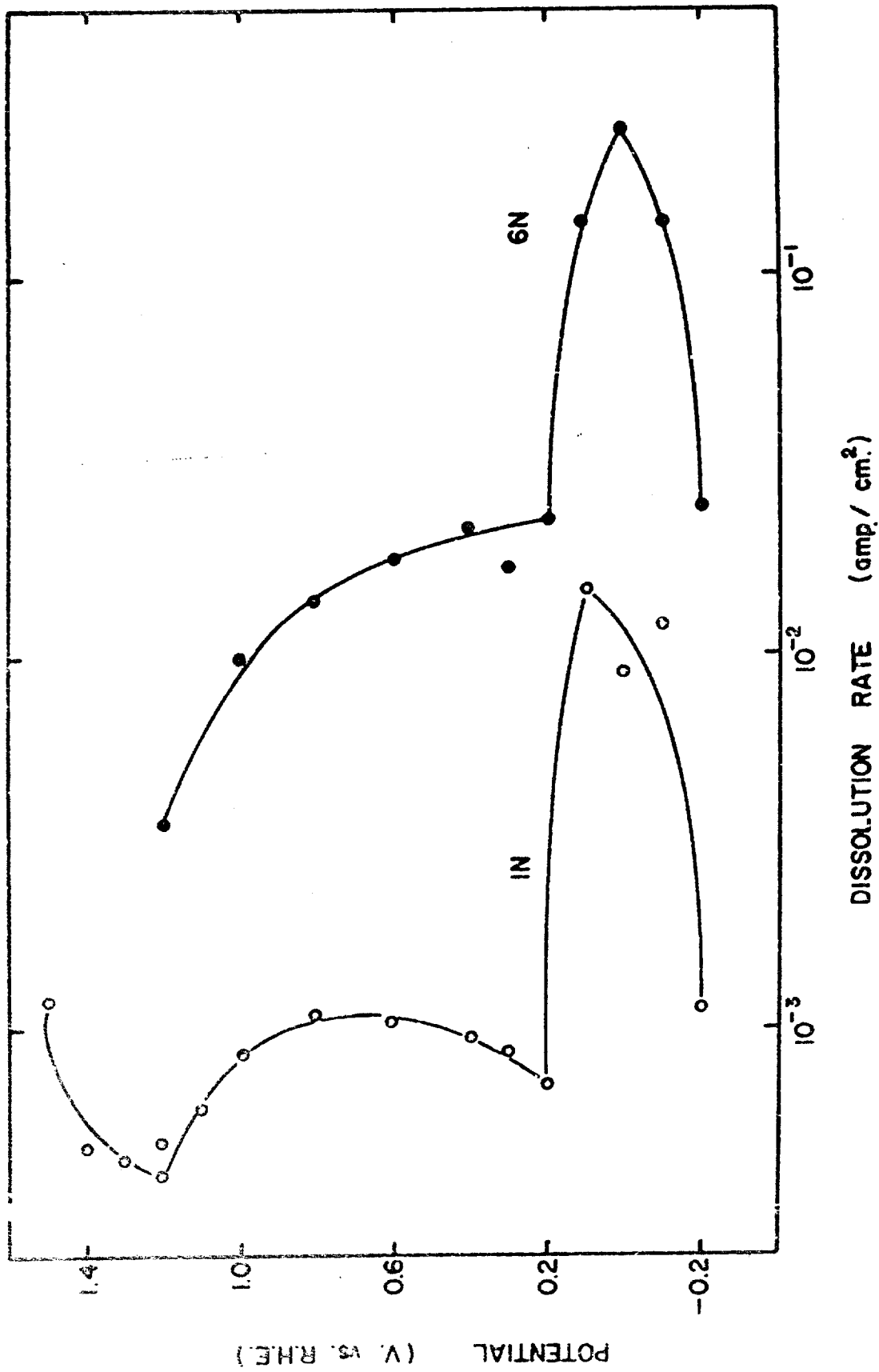


Fig. 5 Anodic Dissolution of 89 Zn - 11 Co in KOH at 30°C, without stirring

A typical active-passive transition is observed in N KOH at about + 0.1 v and 15 mA/cm^2 ; in 6N KOH, the critical potential and current are 0.0 v and 250 mA/cm^2 , respectively. The currents are extremely steady: generally, the current at the end of 3 min was the same as that after 30 min at any given potential. Even for long times, no appreciable change in the current is observed; (e.g. after 15 hrs at 1.2 v in N KOH, the current changed from 4.0 to $5.0 \times 10^{-4} \text{ amp/cm}^2$).

Activation of the 89 Zn - 11 Co alloy was relatively easy even in N KOH. Starting at 1.2 v (passive current $5.0 \times 10^{-4} \text{ amp/cm}^2$ after 15 hrs), a cathodic pulse of 300 mA/cm^2 was applied. The visible oxide layer "peels off" and the passive layer is presumably also reduced. The potential was stepped to zero after 15 sec, and the current observed as a function of time: It is initially higher than in the steady state and slowly drops to the values given in Fig. 5. For example, after 1 min at 0.0 v, the current was 19 mA/cm^2 ; after 2 min, 15 mA/cm^2 . These values are to be compared with the steady-state value of 11 mA/cm^2 given in Fig. 5.

Although the passive characteristics of the 89 Zn - 11 Co alloy are much improved over those of pure zinc, the passive currents in both N and 6N KOH are too large for the intended application. Further studies of the Zn-Co system are intended, particularly of the γ_2 -phase and of electrolyte additions to minimize Co oxide solubility.

6. Zinc-Nickel Alloys

It is known that Ni has good corrosion resistance to alkaline solutions, and therefore, we carried out an examination of the corrosion of Zn-Ni alloys. Figure 6 shows the current-potential curve (10 min points) for 80 Zn - 20 Ni in 6N KOH. The open circuit potential was - 0.135 v. The currents in the active region were fairly steady; e.g. at 0.1 v there was < 10% change from 1 min to 5 min.

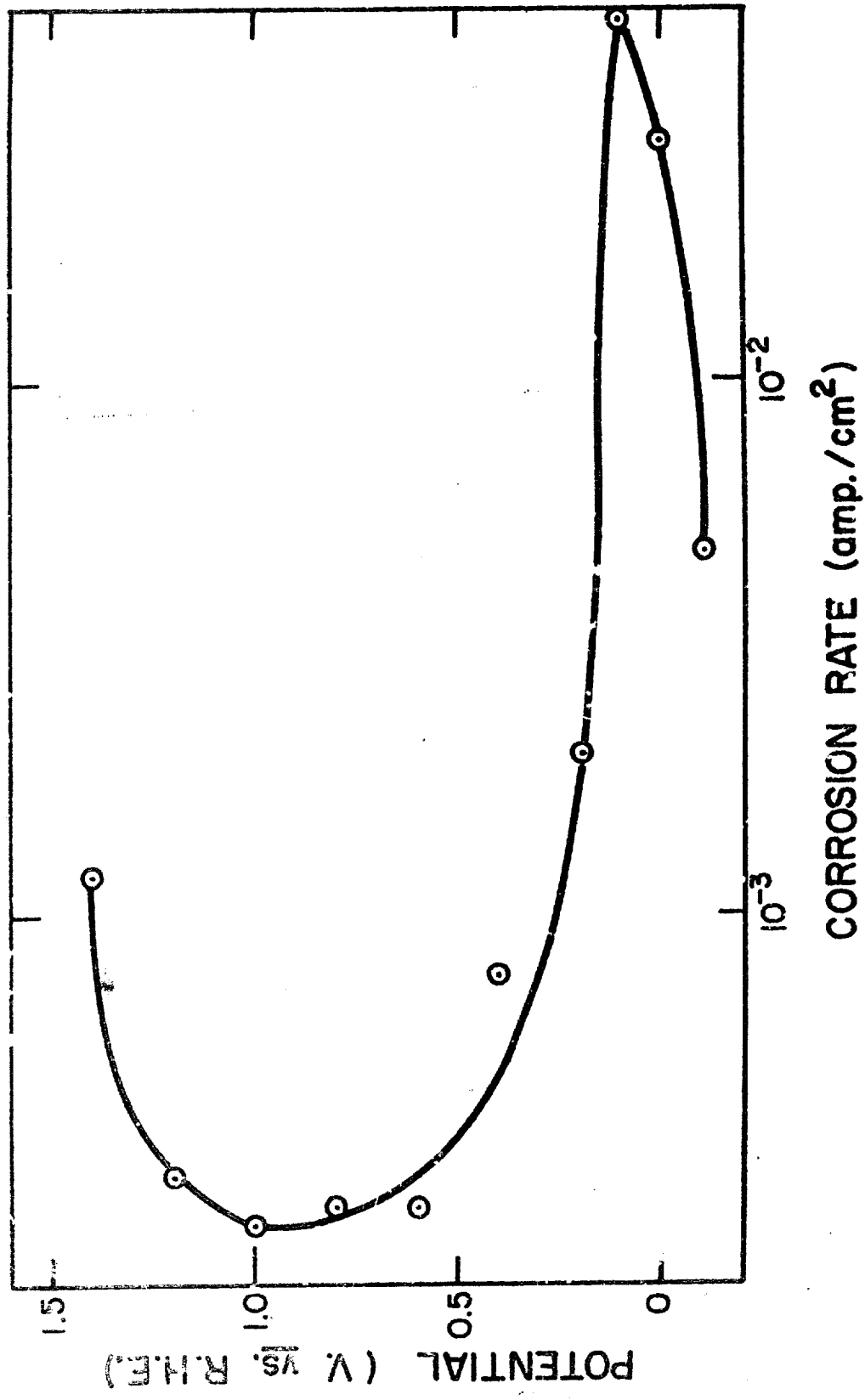


Fig. 6 Anodic Dissolution of 80 Zn - 20 Ni in 6 N KOH at 30°C, without stirring.

In the passive region the decay of current was greater and at 0.7 v, for example, the current fell 40% from 1 min to 5 min and another 30% from 5 min to 10 min. The active dissolution of the alloy is quite good ($i_c \sim 50 \text{ mA/cm}^2$) although not quite as good as the Co alloy in 6N KOH (Fig. 4) and at a higher potential (+ 0.1 v vs 0.0 v). The electrode became black in the active region and some H_2 was evolved. Examination of the surface showed that this evolution appeared to occur on specific parts of the surface, perhaps at grain boundaries.

After 15 hours at 1.0 v, the passive current fell to $80 \mu\text{A/cm}^2$, which is $\sim 1/3$ of that for the Co alloy in 6N KOH ($210 \mu\text{A/cm}^2$). The critical current for the alloy (50 mA/cm^2) was 0.14 that of Zn in 6N KOH and the passive current was ~ 0.0014 that of Zn. The ratio of i_c/i_p (600:1) is a little better than that of the Co alloy.

The anodic behavior of the 80 Zn - 20 Ni alloy in 1, 3, and 6N KOH at 30°C is shown in Fig. 7. The critical potential (vs RHE) is essentially independent of the KOH concentration. In other words, it shifts to more noble values in the same way as the reversible hydrogen electrode ($\sim 60 \text{ mv}$ per unit change in activity of KOH). The critical current increases with KOH concentration from about 6.0 mA/cm^2 in N KOH to 50 mA/cm^2 in 6N KOH. The passive current also increases with KOH concentration from about 0.055 mA/cm^2 in N KOH to 0.25 mA/cm^2 in 6N KOH.

As mentioned above, the passive currents are time-dependent, while the currents in the active region are not. For example, in 6N KOH the passive current decreases from the value given above ($250 \mu\text{A/cm}^2$) to $80 \mu\text{A/cm}^2$ in 15 hrs. In N KOH and at a fixed potential of 0.80 v, the passive current decreases from $55 \mu\text{A/cm}^2$ to $32 \mu\text{A/cm}^2$ in 16 hours.

It should be pointed out that, in general, the passive current is expected to decrease as a function of the logarithm of time. This is because the passive film thickens according to a direct logarithmic relation for most metals and alloys. Therefore, the values given

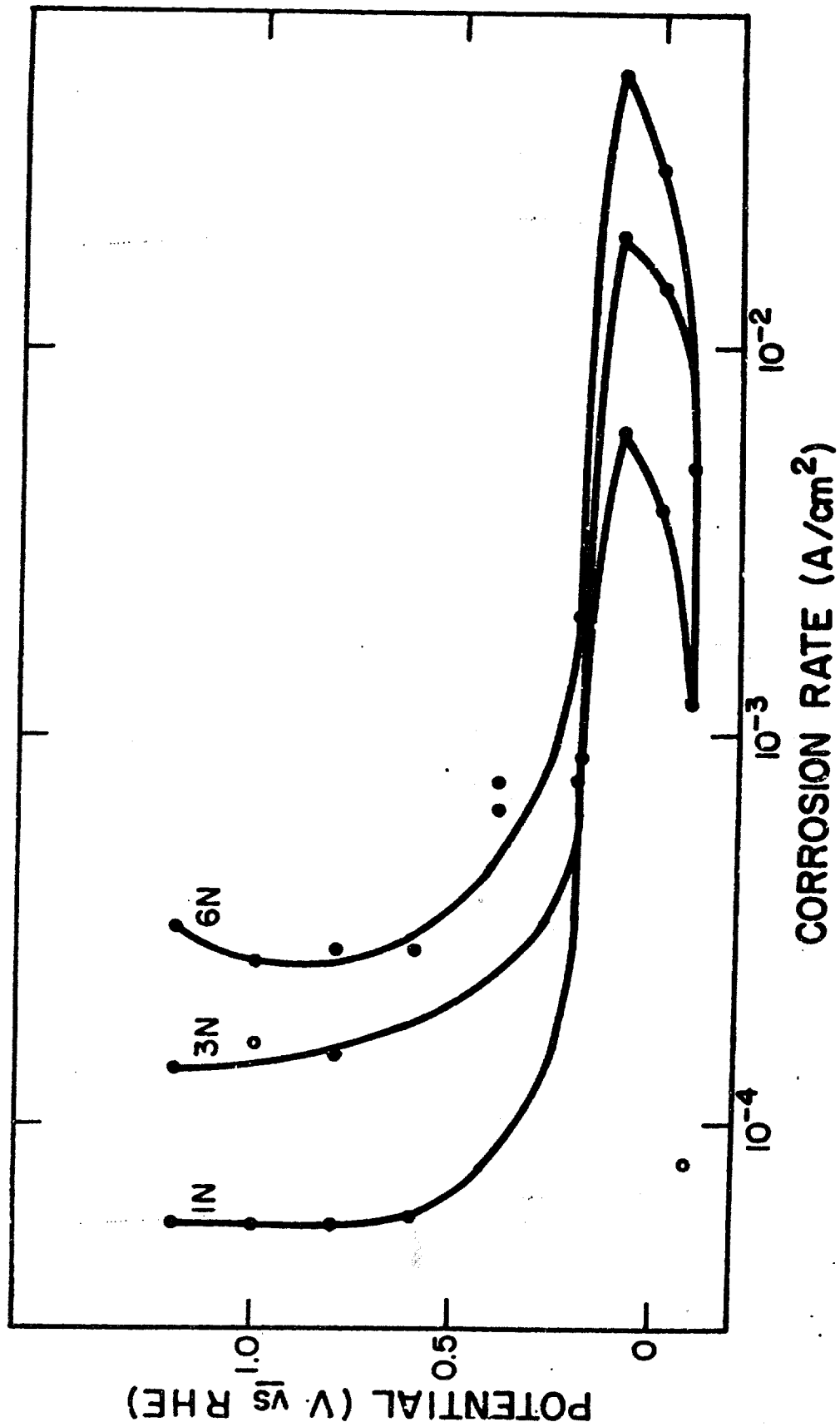


Fig. 7 Anodic Dissolution of 80 Zn - 20 Ni in KOH at 90°C, without stirring

above are upper limits to the passive current expected during the course of an extended period of time - for example, a year.

Activation of 80 Zn - 20 Ni Alloys The activation characteristics of passivated 80 Zn - 20 Ni alloys in N KOH were studied in detail. Cathodic chronopotentiograms, obtained at a cathodic current density of 200 mA/cm^2 , are shown in Fig. 8 for alloys passivated at 0.8 and 1.2 v. It is evident that no reduction plateau exists for alloys previously passivated at 0.8 v, while a very distinct potential arrest appears with alloys passivated at 1.2 v. Since it is clear from the anodic curve that a passive film is present at 0.8 v, we conclude that the passive layer formed at relatively low potentials is difficult to reduce. On the other hand, the passive film formed at higher potentials is apparently more easily reducible.

Similar results were observed in 3N KOH. In 6N KOH a potential plateau, corresponding to oxide reduction, is apparent after passivation both at 0.8 and 1.2 v.

Preliminary experiments showed that it was relatively difficult to activate alloys in 1 and 3N KOH by cathodic pulses of the order of 200 mA/cm^2 . Accordingly, the activation characteristics were studied in 6N KOH.

Figure 9 presents results on the activation of 80 Zn - 20 Ni in 6N KOH solutions. In each case the electrode was passivated first at 0.5 v until the passive current density was $300 \text{ } \mu\text{A/cm}^2$ (generally requiring about 15 min), then the potential was increased to values between 1.45 and 1.6 v for 60 sec, and then it was lowered to 0.0 v vs RHE and the current observed as a function of time. Figure 9 shows the ratio of the current obtained after the sequence described above, to the current obtained at 0.0 v for a fresh surface of the same electrode. The ratio can be considered as a percent activation and is, in fact, so denoted on the figure.

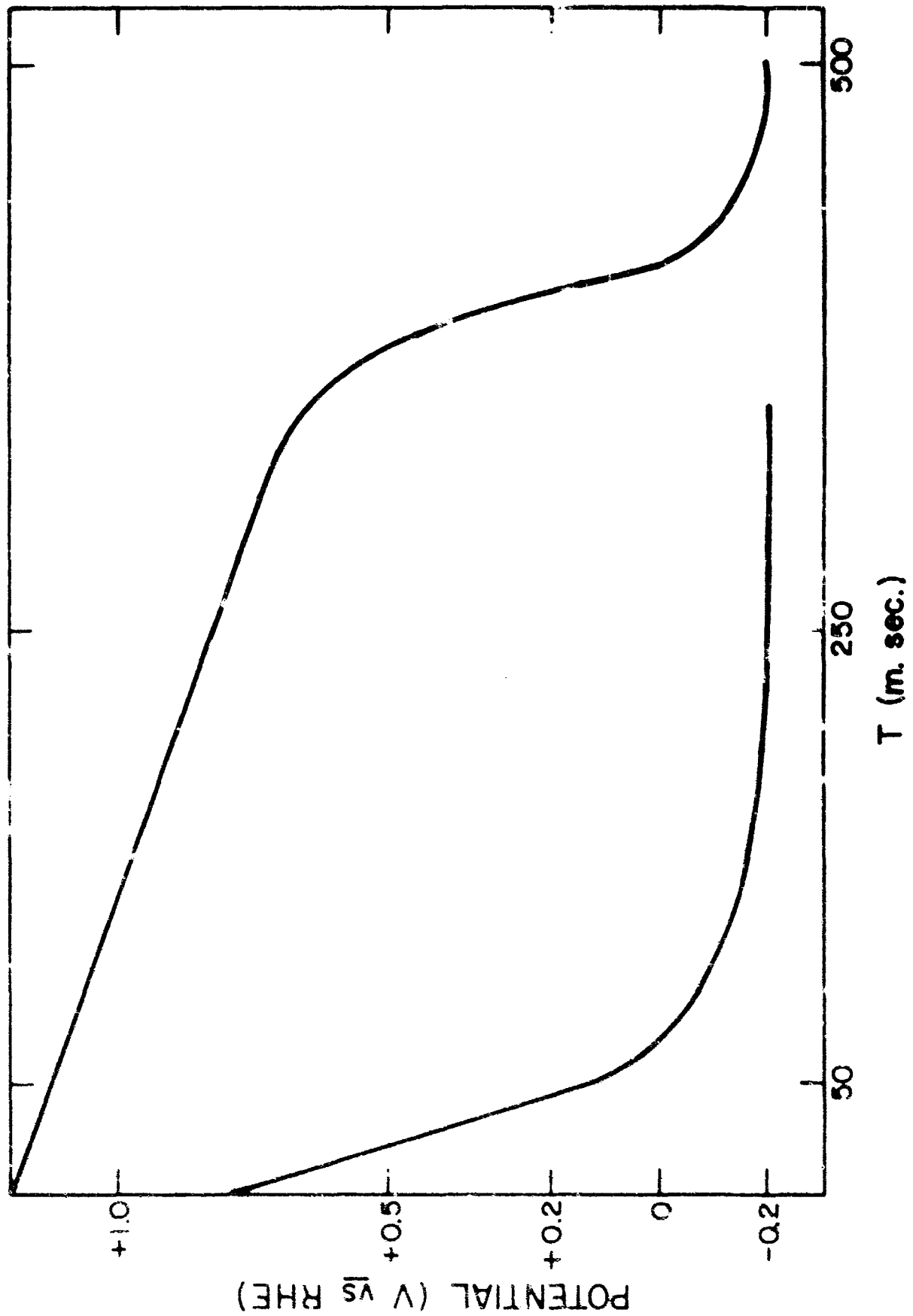
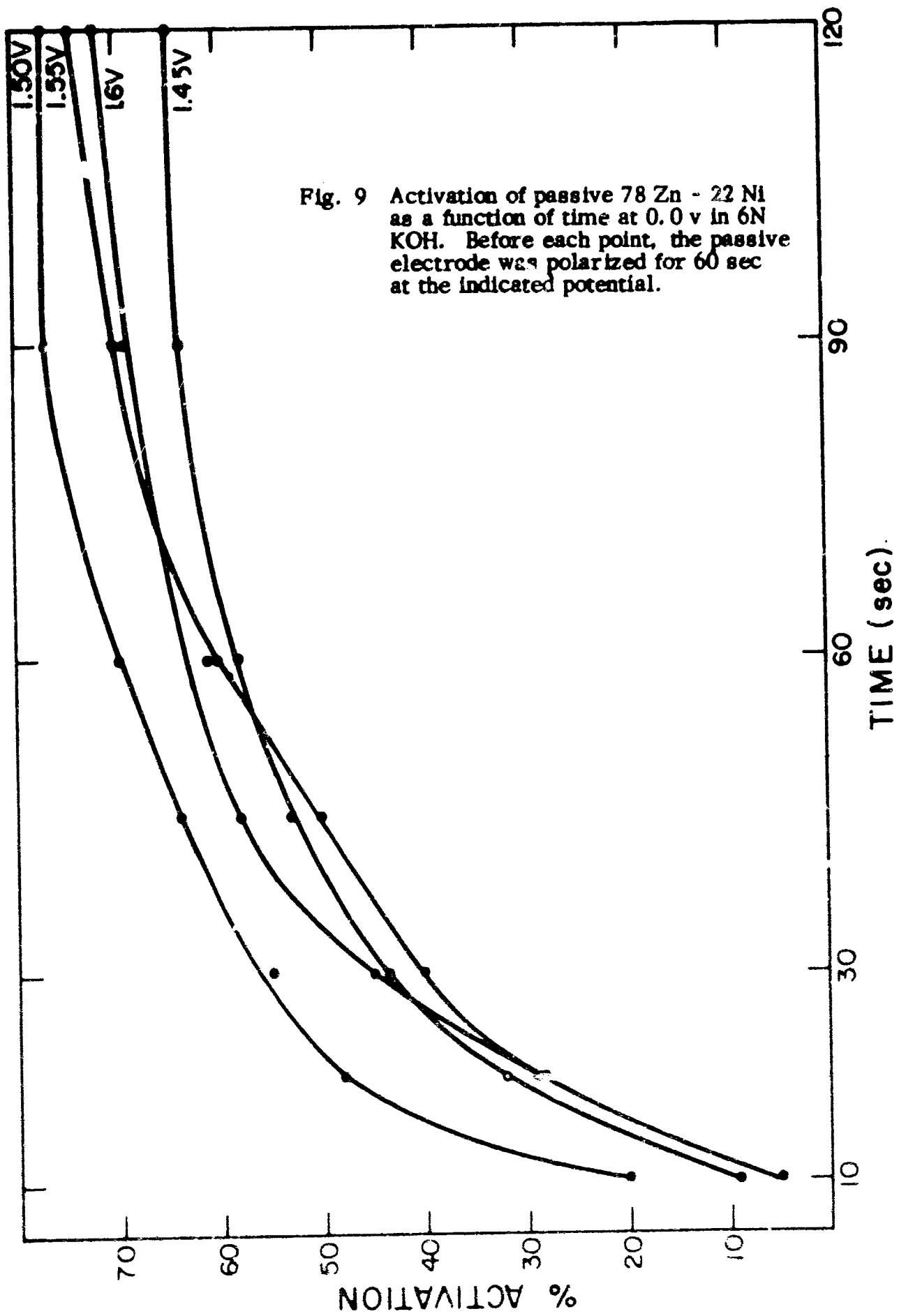


Fig. 8 Cathodic chronopotentiograms (200 mA/cm²) of 80 Zn - 20 Ni in 6N KOH from 0.8 and 1.2 v.



The results show that anodic pretreatment of a passive electrode leads to activation (~ 70%) in times between 20 and 60 sec. There are some differences between the lowest and the highest potentials used, but these are relatively minor. Figure 10 shows the effect of time at the second potential, in this case 1.6 v, on the ease of activation. The potential sequence was the same as in Fig. 8, but now the electrode was left at the more positive potential for times varying between 5 and 60 sec. The figure shows that the ease of passivation increases the longer the electrode is pre-polarized at 1.6 v. Under the best conditions, 60 sec at 1.6 v, 75% of activation is achieved in a total time of 90 sec (60 sec at 1.6 v and 30 sec at 0.0 v).

The reproducibility of these results is illustrated in Fig. 11 which shows a duplicate series of runs for 20 and 30 sec at 1.6 v. In general, active currents were reproducible to about 10%.

7. Summary of Characteristics of Zn Alloys

The results with zinc and zinc alloys in N and 6N KOH are summarized in Table II. Alloying, in general, shifts the dissolution curve in the active region to more positive potentials; the critical passivation potential is also displaced to more positive values. The passive current is decreased by factors up to 100. Long-term currents show even greater differences since the passive current on zinc is not time-dependent, while for the most promising alloys, it decays with time.

B. Alternatives to the Zinc Anode

In addition to the zinc alloys discussed above, we have briefly considered the possibility of using other elements as the negative electrode in the alkaline battery.

1. Chromium

One metal with well-known, active-passive characteristics is Cr and, while it is not suitable for alloying with Zn, it could

Table II

Critical Potential and Currents and Passive Currents of Zn Alloys

(30.0°C)

<u>Electrode</u>	<u>Critical Potential</u>	<u>Critical Current</u>	<u>Passive Current (at 0.6 to 0.8 v)</u>
Zn (1N KOH)	-0.1 v	32 ma/cm ²	7 ma/cm ²
Zn (6N KOH)	-0.2 v	275 "	80 "
80 Zn-20 Ni (1N)	+0.1 v	6 ma/cm ²	0.07 ma/cm ²
80 Zn-20 Ni (6N)	+0.1 v	50 "	0.3 "
78 Zn-22 Co (1N)	0.0 v	7.5 ma/cm ²	0.1 ma/cm ²
78 Zn-22 Co (6N)	0.0 v	110 "	2.8 "
89 Zn-11 Co (1N)	+0.1 v	15 ma/cm ²	1.0 ma/cm ²
89 Zn-11 Co (6N)	0.0	240 "	18 "
90 Zn-10 Fe (6N)	0.0	45 ma/cm ²	20 ma/cm ²
83 Zn-17 Mn (1N)	< -0.2	~ 3 ma/cm ²	2 ma/cm ²

Note: Values given for current are generally at the end of 5 min.

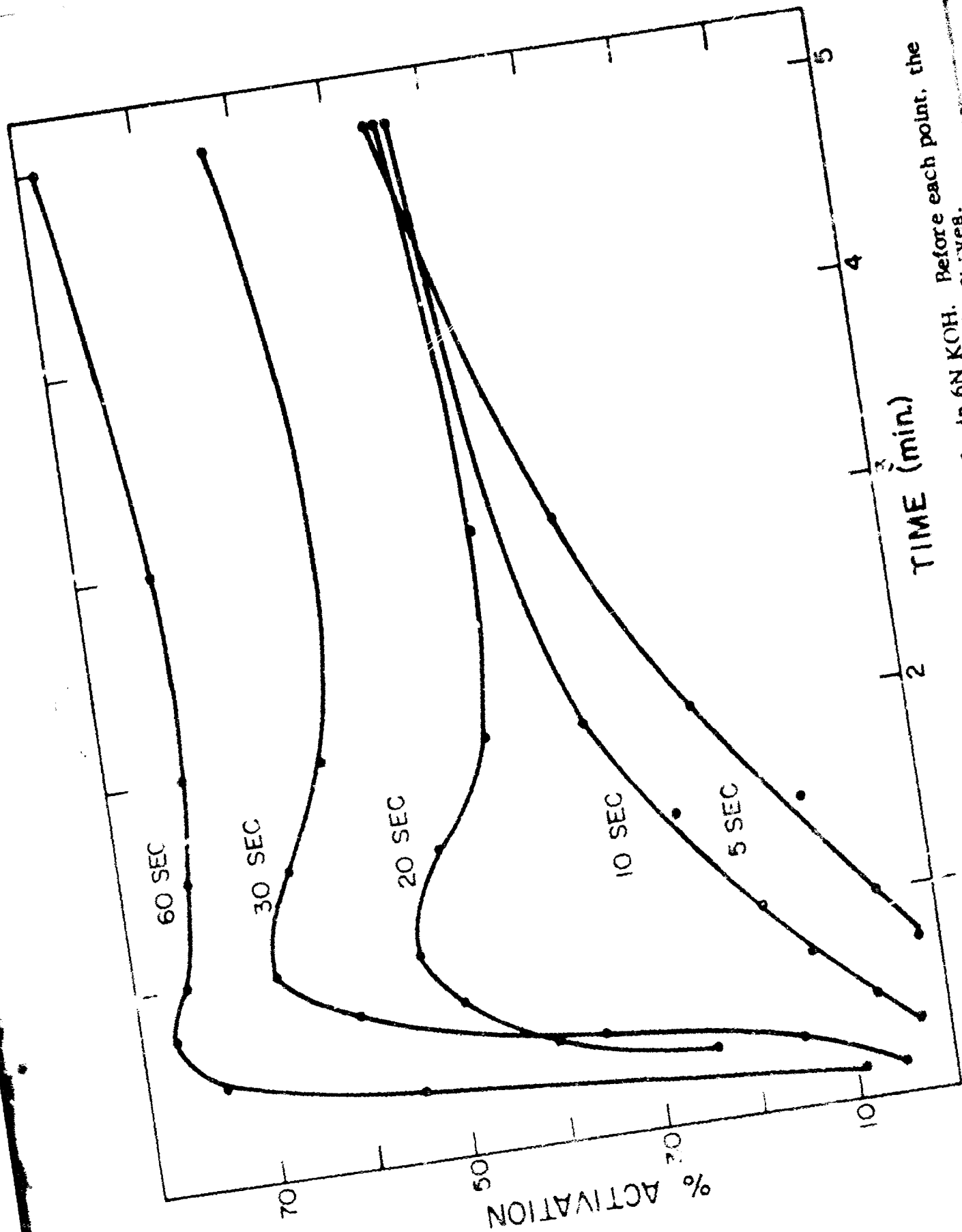


Fig. 10 Activation of $^{78}\text{Zn}-^{22}\text{Ni}$ as a function of time at 0.0 v in 6N KOH. Before each point, the passive electrode was polarized to 1.6 v for a time indicated on the curves.

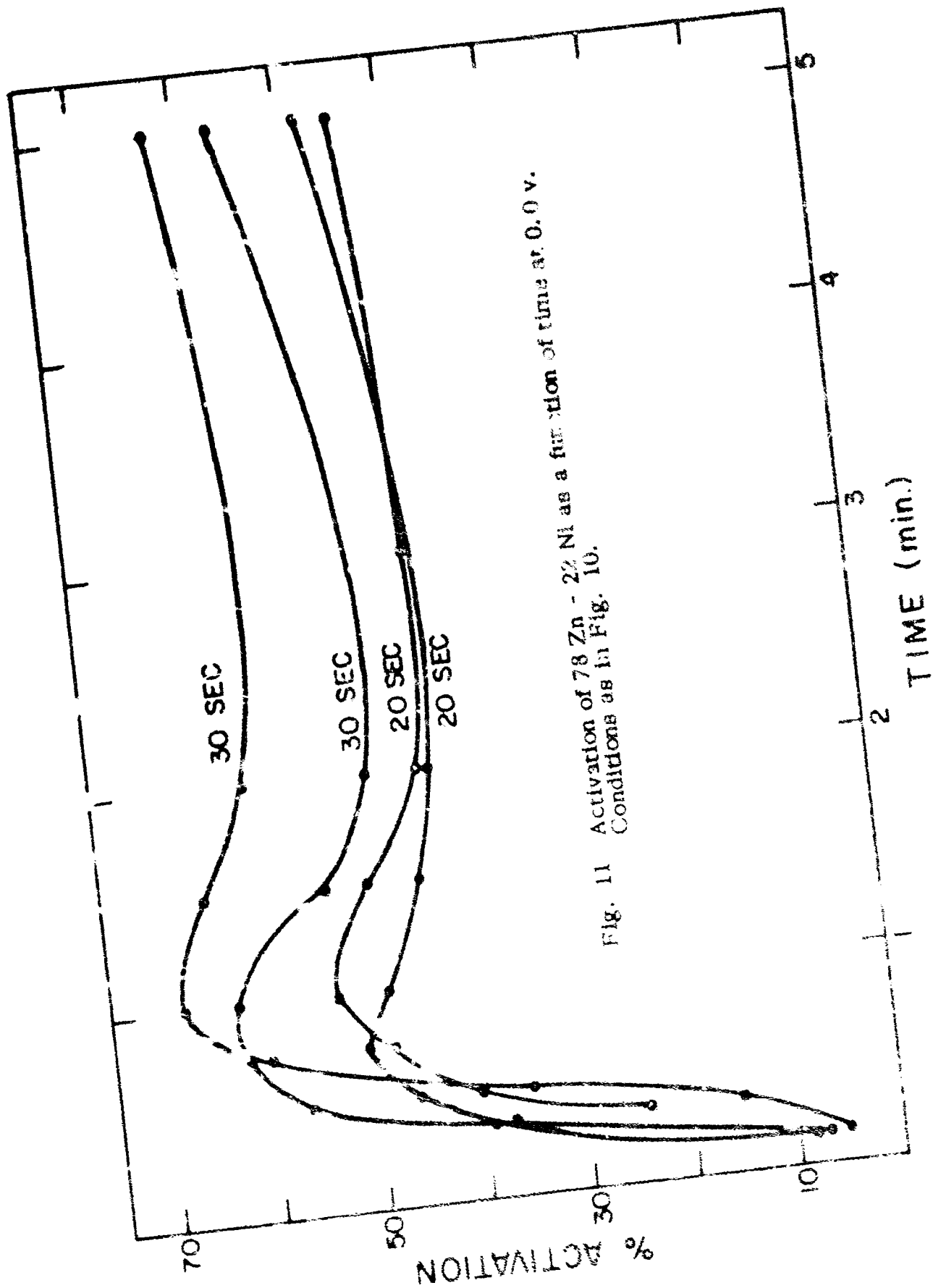


Fig. 11 Activation of 78 Zn - 2% Ni as a function of time at 0.0 V.
 Conditions as in Fig. 10.

conceivably replace it. Figure 12 shows the dissolution of Cr in 1N and 6N KOH. In both cases the active dissolution of Cr was absent and the open circuit potential was well into the passive region. Dissolution was reasonably rapid above this, but transpassive. Even extended cathodic pretreatment (-0.6 v for 2 hours, where ~ 20 mA/cm² of H₂ were evolved) failed to give more than a transitory active dissolution region. Addition of 0.1 M KCl (an excellent passive-film destroyer) to the 6N KOH electrolyte was not successful in revealing an active dissolution region for Cr. We conclude then that Cr is not suitable as an anode material for the alkaline cell.

2. Aluminum

Aluminum is another possible substitution for Zn; the rapid corrosion of this element in alkali is well-known. We have already indicated that Al is not suitable for our purpose as an anode in acid solutions because it is transpassive and because it shows considerable H₂-evolution under discharge. In alkaline solutions (Fig. 13) the Al is also apparently transpassive, although the rapid H₂-evolution under discharge is not seen. H₂-evolution at open circuit (-0.98 v) is apparently ~ 1 mA/cm² (Fig. 14) and, in fact, dissolution is obviously occurring below open circuit so that the evolution is a little higher than shown in Fig. 14. Galvanostatic charging, both anodic and cathodic, showed the presence of films on the surface which could be brought to considerable thickness (several coulombs/cm²) but which readily dissolved on subsequent potential displacement to 0.0 v. However, the obvious transpassive behavior of Al in alkaline solutions (Fig. 13) rules it out for our purpose.

3. Magnesium

The Mg anode is of interest because of its theoretical high energy density. In particular, the anode potential is so low that one could couple this anode with the m-dinitrobenzene cathode (the

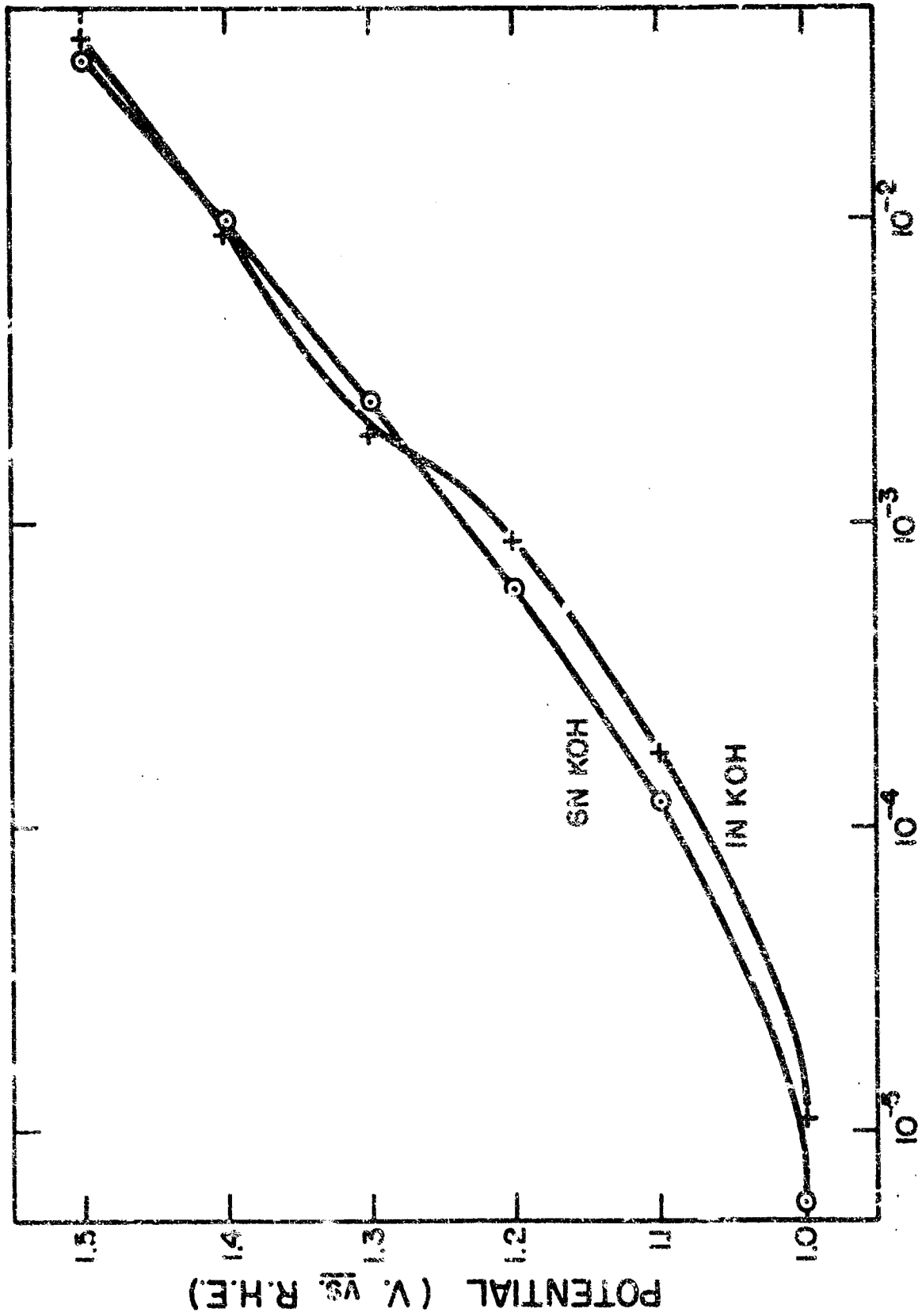
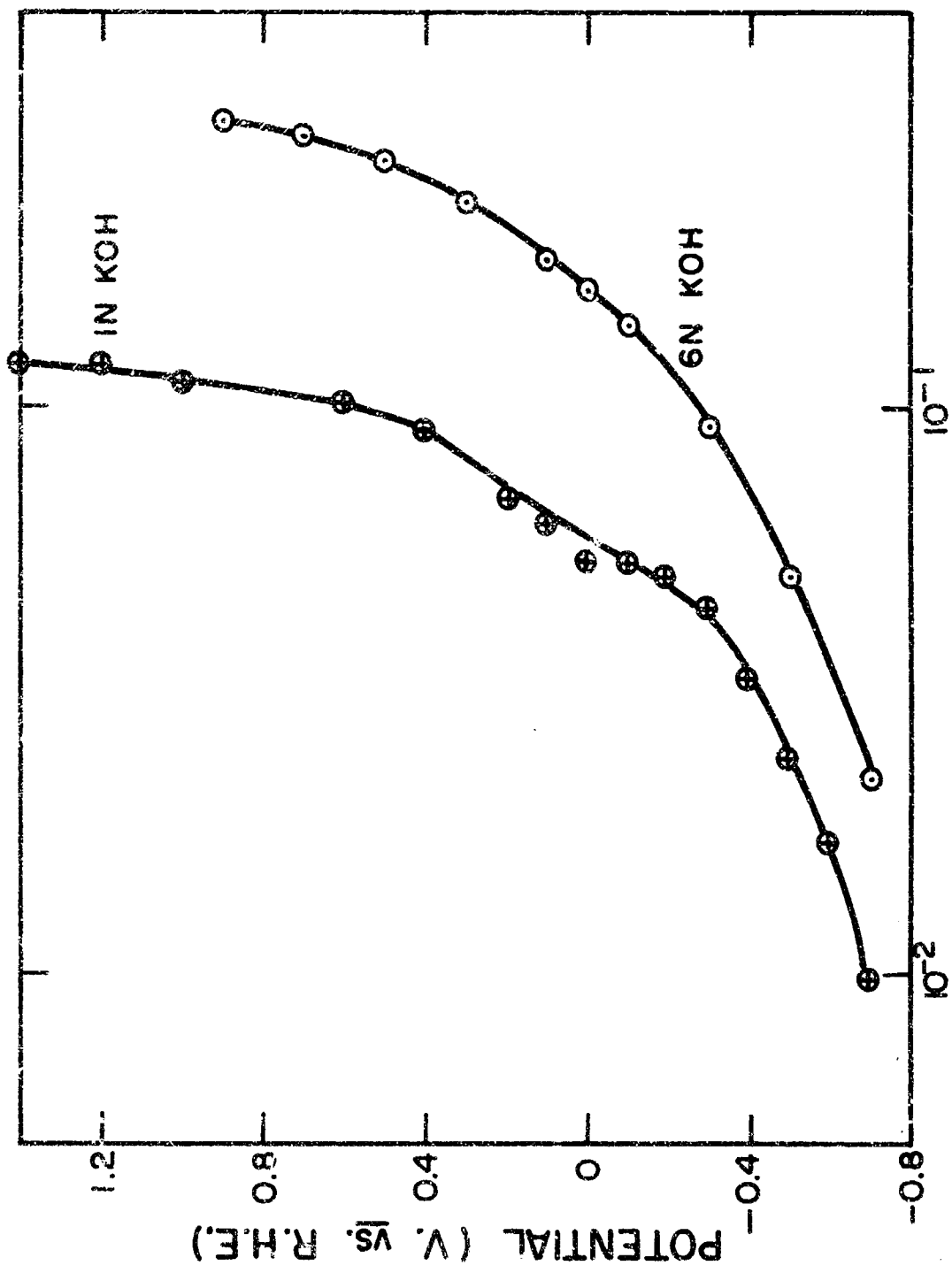


Fig. 12 Anodic Dissolution of Cr in KOH at 30°C, unstirred.



CORROSION RATE (cm²/cm²)

Fig. 13 Anodic Dissolution of Al in KOH at 30°C, unstirred.

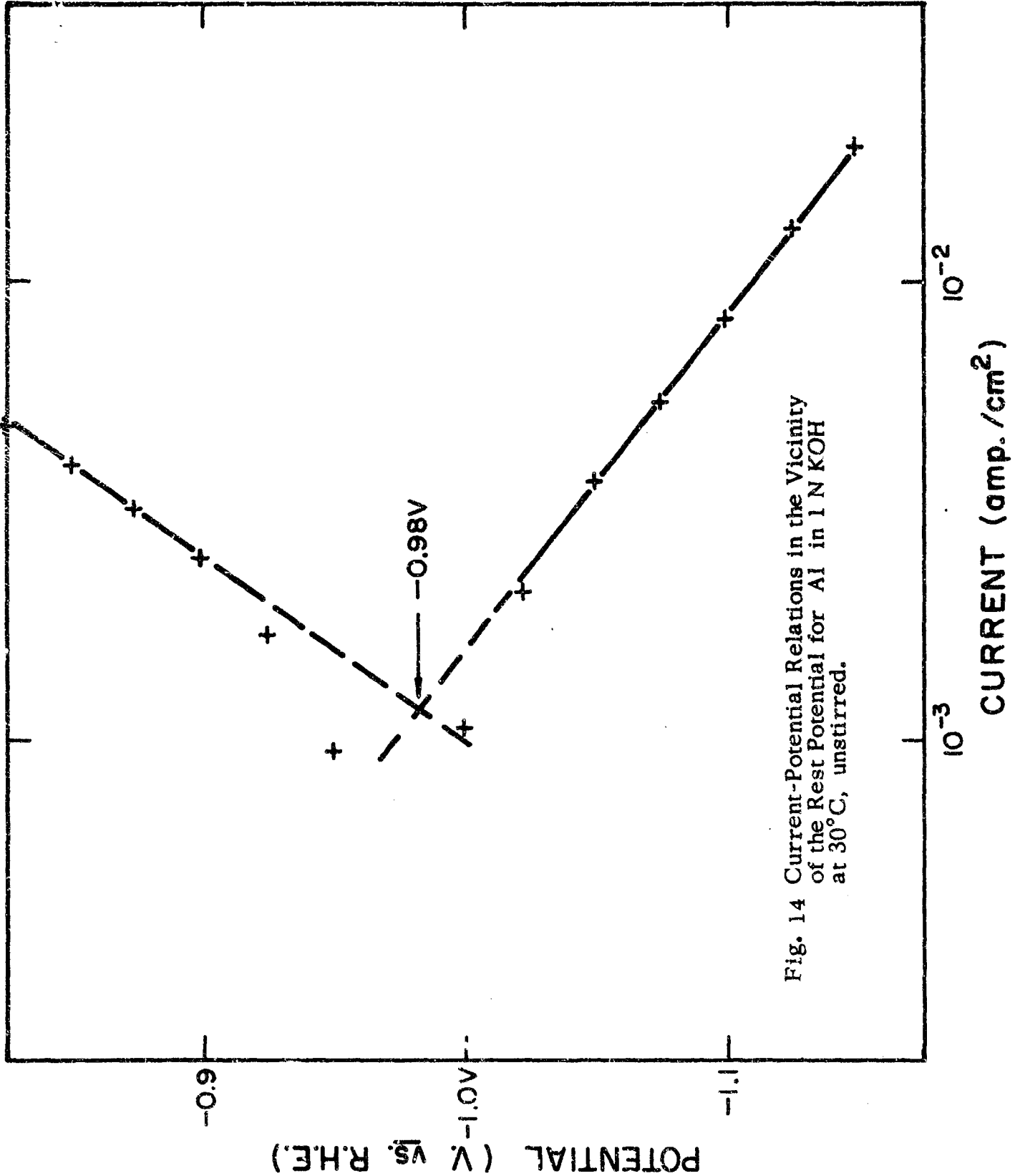


Fig. 14 Current-Potential Relations in the Vicinity of the Rest Potential for Al in 1 N KOH at 30°C, unstirred.

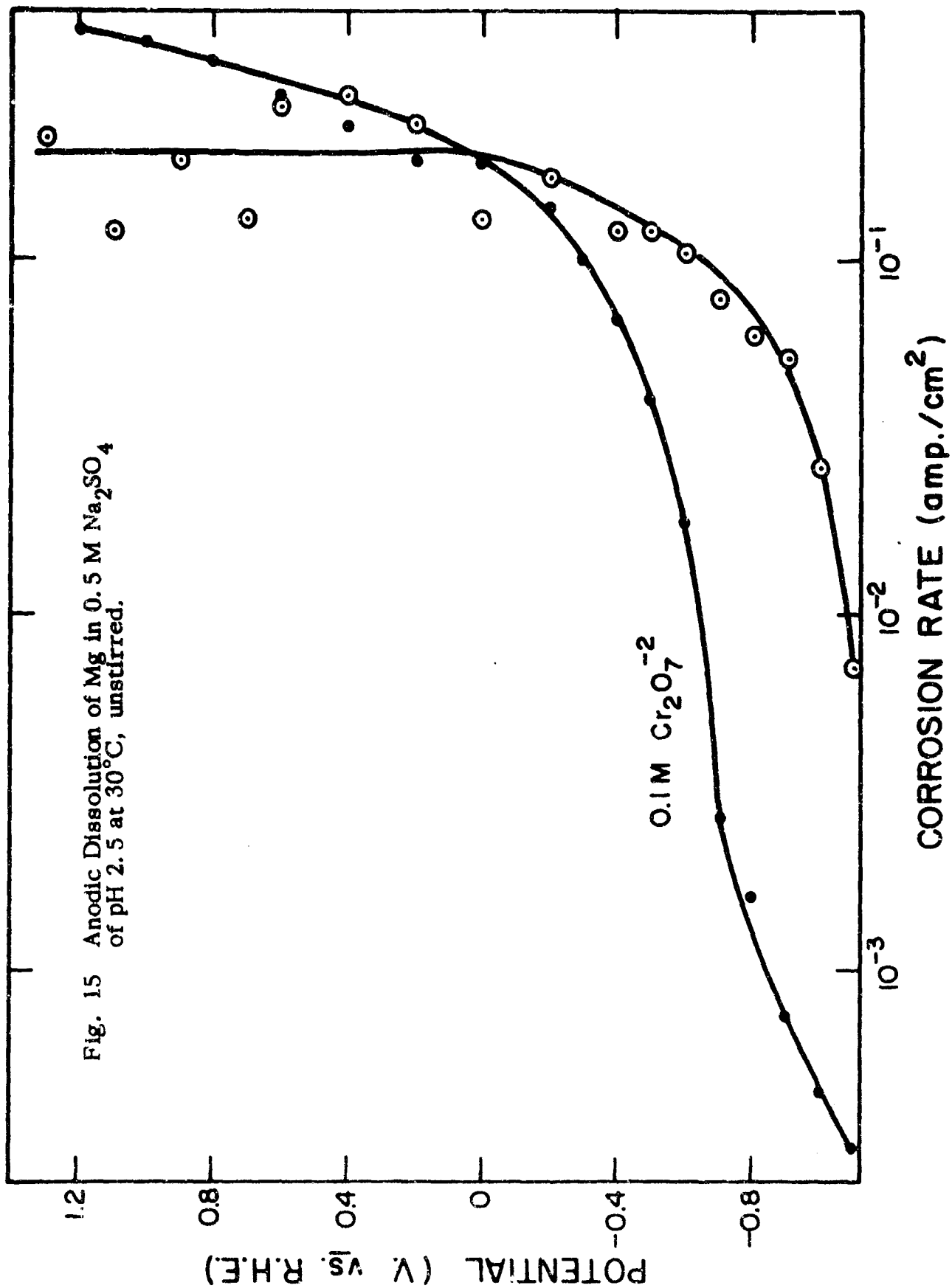
potential of which is only a few tenths of a volt positive of H^+/H_2 . We have continued an investigation of Mg in acid solution (Fig. 15) and we conclude that elemental Mg is transpassive and therefore unsuitable for our purpose. Addition of $Cr_2O_7^{=}$, which is reported to improve the corrosion resistance of Mg, did not change the character of the curve (Fig. 15).

An alternative to electrochemical passivation is plating the Mg with Cu, as we have done with Zn. Preliminary experiments have shown great difficulty in obtaining a coherent plate.

Another way of improving the Mg anode is combining it with a high H_2 -overvoltage material, e. g. Hg or Cd. This would lower the open circuit corrosion rate and would tend to eliminate the negative difference effect (H_2 -evolution on discharge). Attempt was made to amalgamate the Mg. Acid-pickled Mg was dipped into Hg at $200^\circ C$ and the corrosion of the resulting solution of Mg in Hg (up to about 2M in Mg) was examined. It turned out that the Mg in Hg diffuses to the surface of the solution and oxidizes even in air. The amalgam did not form a coherent protective film, as does Mg itself in air, and consequently the amalgam rapidly defoliated, i. e. formed thick layers of a reaction product (MgO , or $Mg(OH)_2$, or, perhaps, Mg_3N_2) on its surface. Rapid H_2 -evolution was found even at open circuit in 1M KCl and hence the amalgam was not suitable for our purpose. The problem appears to be that Mg oxidizes and dissolves away from the surface of the amalgam. It is intended to investigate this possibility of suppressing the H_2 -evolution of Mg further by examining the behavior of a solid alloy, e. g. a Cd rich Cd-Mg alloy.

C. Mixed Electrolytes

The anodic dissolution curves of the most promising alloys (namely 82 Zn - 18 Co and 80 Zn - 20 Ni) were obtained in N KOH containing sulfate and chloride additions. The purpose of this study is to explore possible electrolyte compositions which will have sufficient conductivity for batteries but at the same time will lead to



more favorable passive currents for the battery anode. We intend to explore systems containing sulfate, perchlorate, chloride, and fluoride and perhaps other salts.

The anodic dissolution curve of the 82 Zn - 18 Co alloy in N KOH and .4M K_2SO_4 (~ a saturated solution) is shown in Fig. 16. If we compare this with the results for the same alloy in the same solution (see Fig. 3) we find small changes in the critical current and passive current, while the critical potential remains essentially unchanged at 0.0 v. The critical current decreases from 7.5 to 5.5 mA/cm², while the passive current increases from 0.1 to 0.15 mA/cm².

Figure 17 gives similar results for this alloy in a solution N in KOH and KCl. Again, the critical potential and the critical current are essentially unchanged. The passive current is also of the same order as in KOH alone. However, the passive current in chloride solutions increases with time, while in KOH, it decays with time. For example, at - 0.6 v the current in N KOH and N KCl increases from 0.045 mA/cm² to 0.12 mA/cm² in 15 hrs. The opposite behavior was observed in KOH. (See arrow in Fig. 3.) The increase of the passive current with time may be due to the well-known tendency of Cl ion to penetrate passive films and, in some cases, produce pits. The behavior of 80 Zn - 20 Ni in solution containing sulfate (Fig. 18) and chloride (Fig. 19) is substantially the same as in N KOH alone. The passive potential remains unchanged at about + 0.1 v and the critical current at between 6 and 8 mA/cm². The passive current is also little affected, being generally about 0.1 mA/cm². It appears that the passive current may be somewhat higher in the solutions containing the inert salt than it is in KOH alone.

The time dependence of the passive current of the Ni alloy in Cl solutions is similar to that in KOH alone (Fig. 19). For example, the current decreases from 0.1 mA/cm² to 0.04 mA/cm² in 1 hr at 0.6 v.

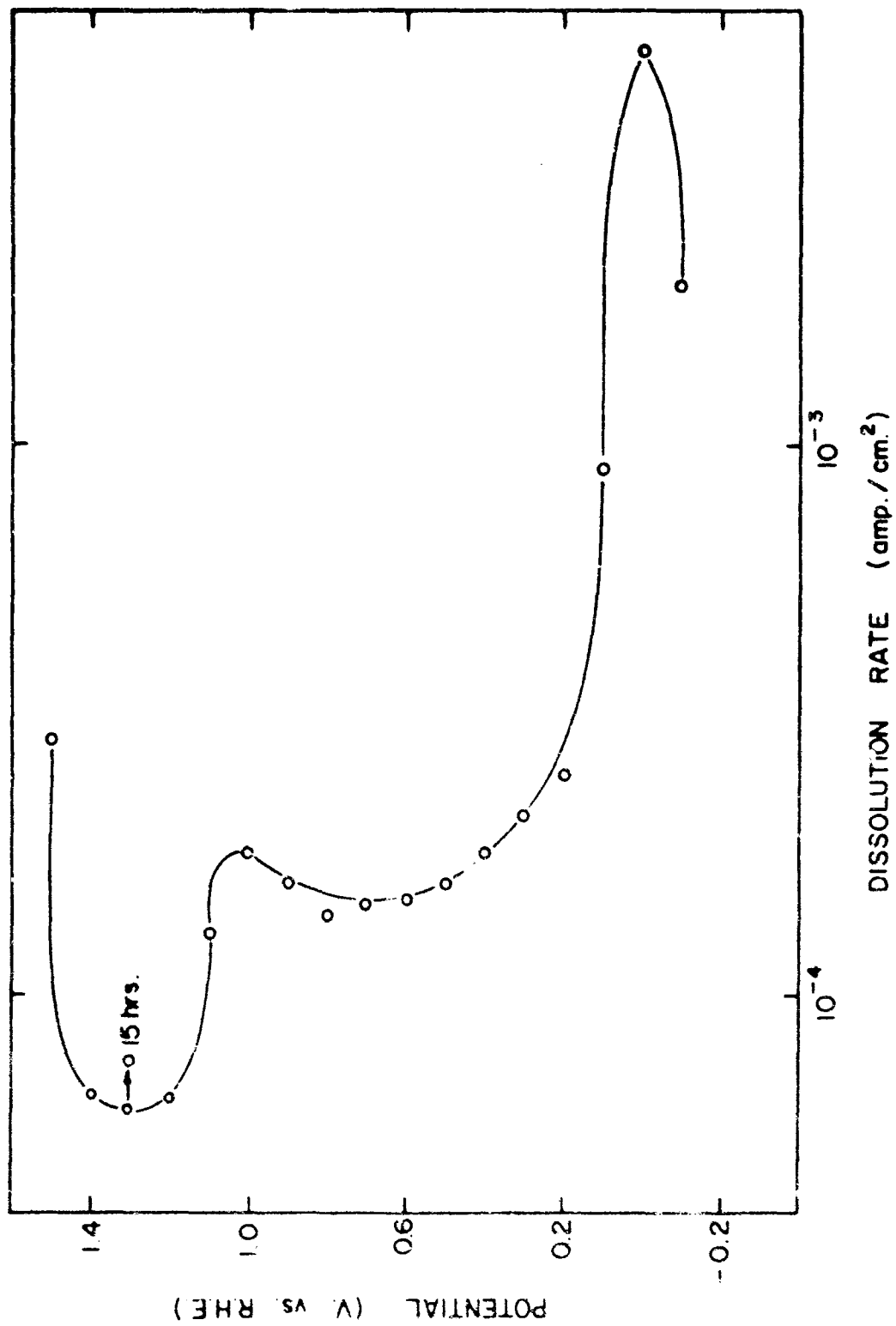


Fig. 16 Anodic Dissolution of 82 Zn - 18 Co in N KOH and 0.4M K₂SO₄ (satd), unstirred

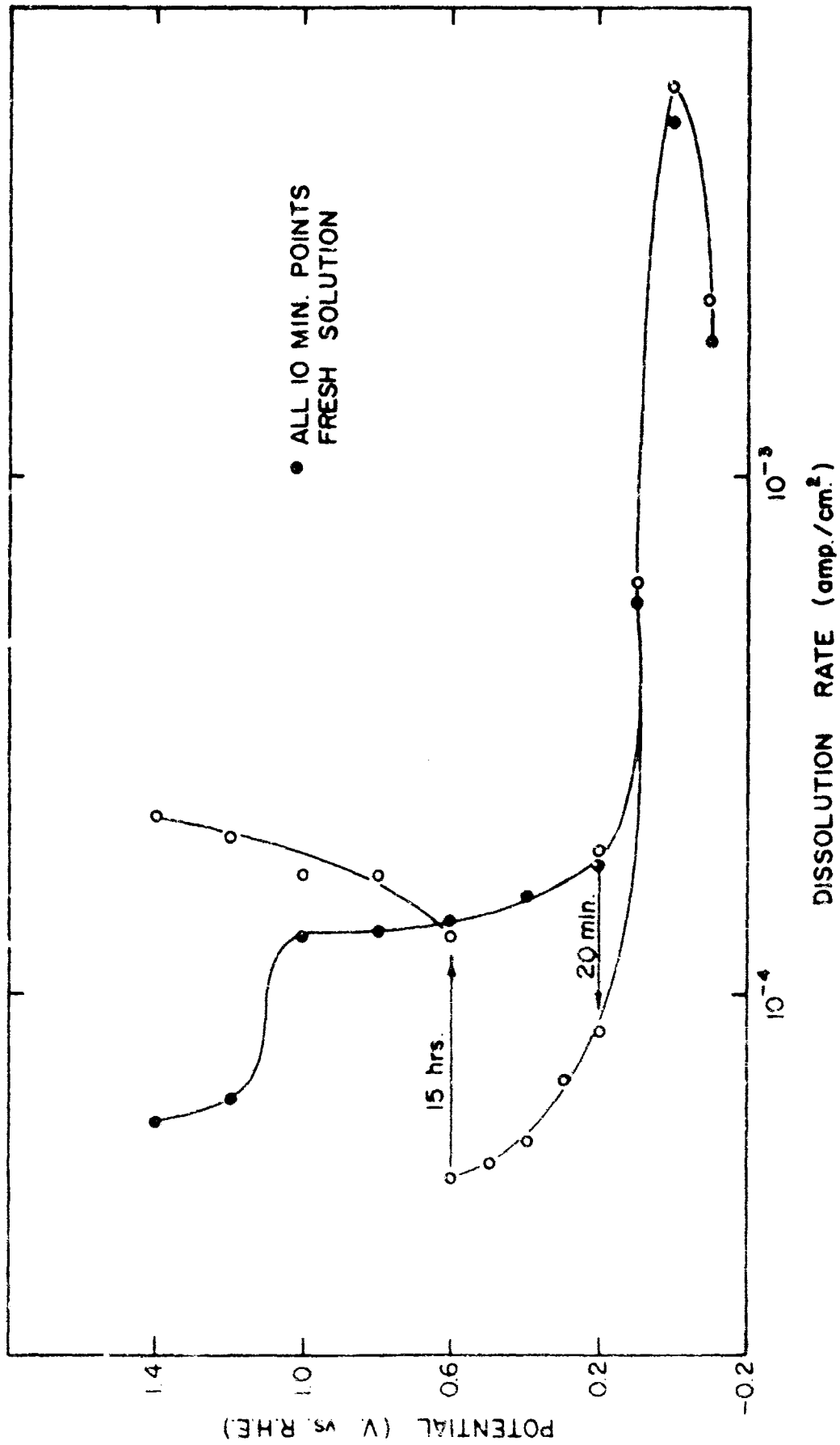


Fig. 17 Anodic Dissolution of 82 Zn - 18 Co in N KOH and M KCl, unstirred

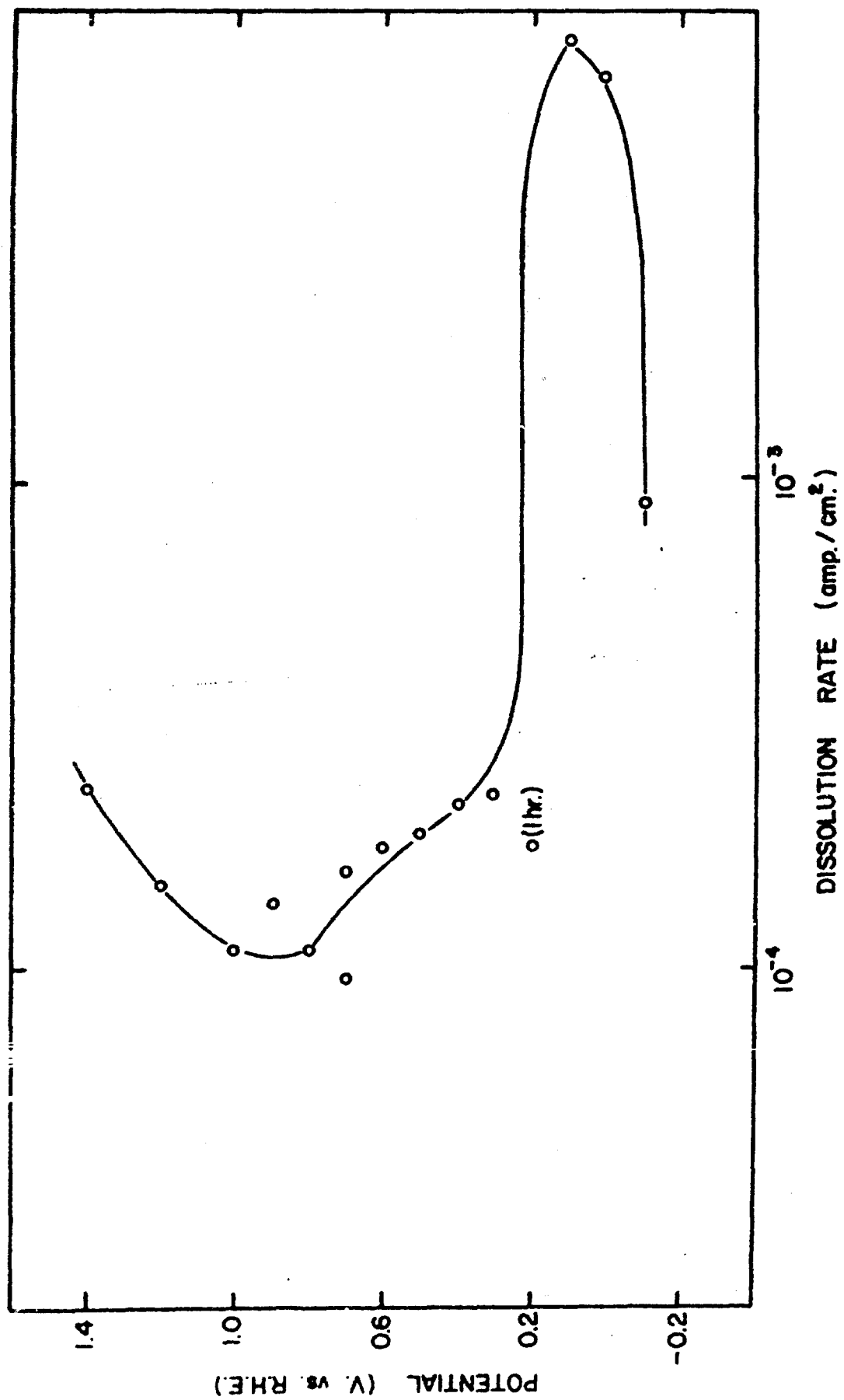


Fig. 18 Anodic Dissolution of 80 Zn - 20 Ni in N KOH and 0.4 M K₂SO₄ (sat'd), unstirred

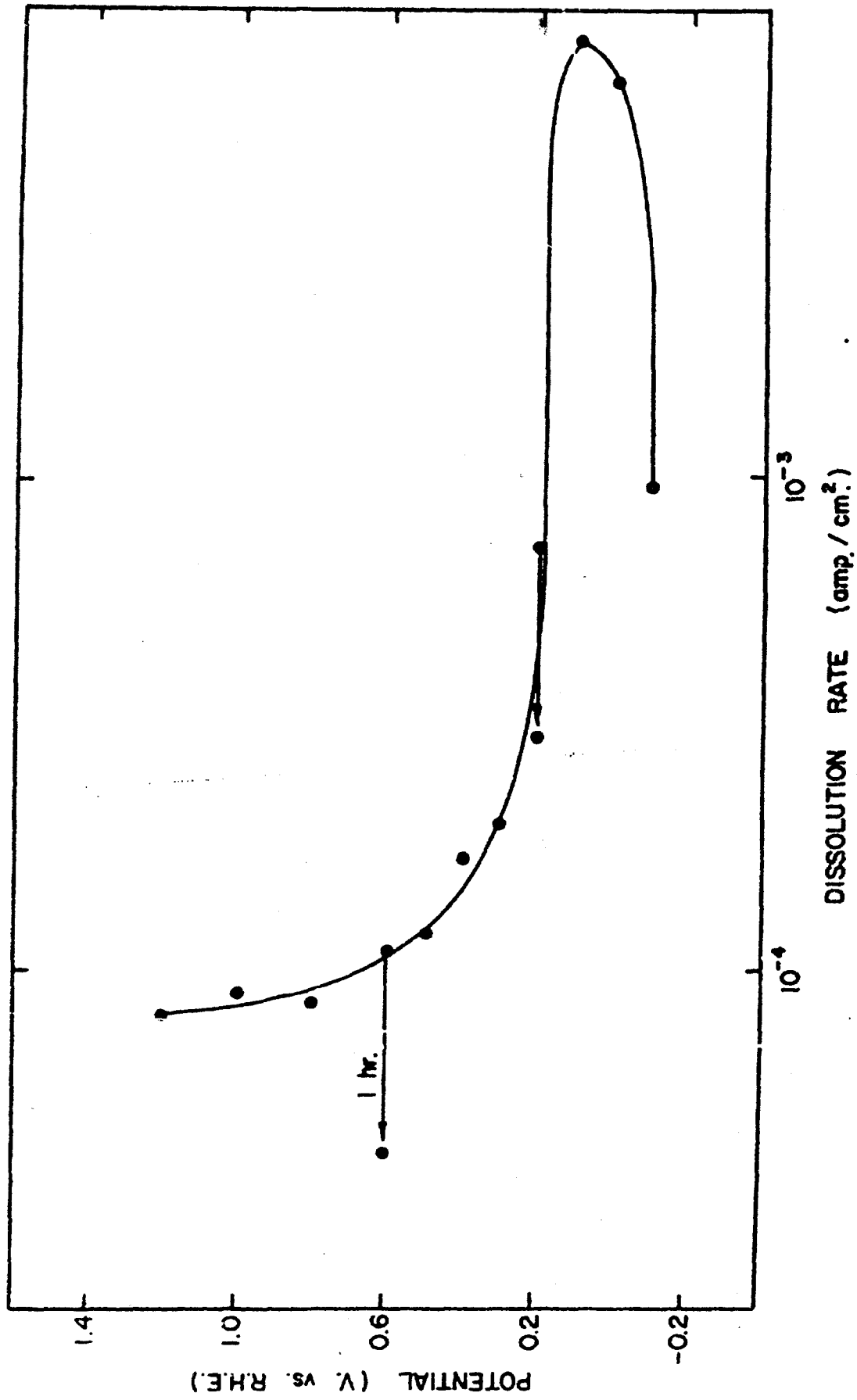


Fig. 19 Anodic Dissolution of 80 Zn - 20 Ni in N KOH and M KCl, unstirred

We have examined briefly the cathodic polarization curve in mixed electrolytes by obtaining hydrogen evolution data. An example of the cathodic polarization curve is shown in Fig. 20 for 80 Zn - 20 Ni in N KOH and N KCl. There is little difference between this curve and the corresponding curve in KOH alone.

The work with mixed electrolytes will continue using both the Zn-Ni and Zn-Co alloys.

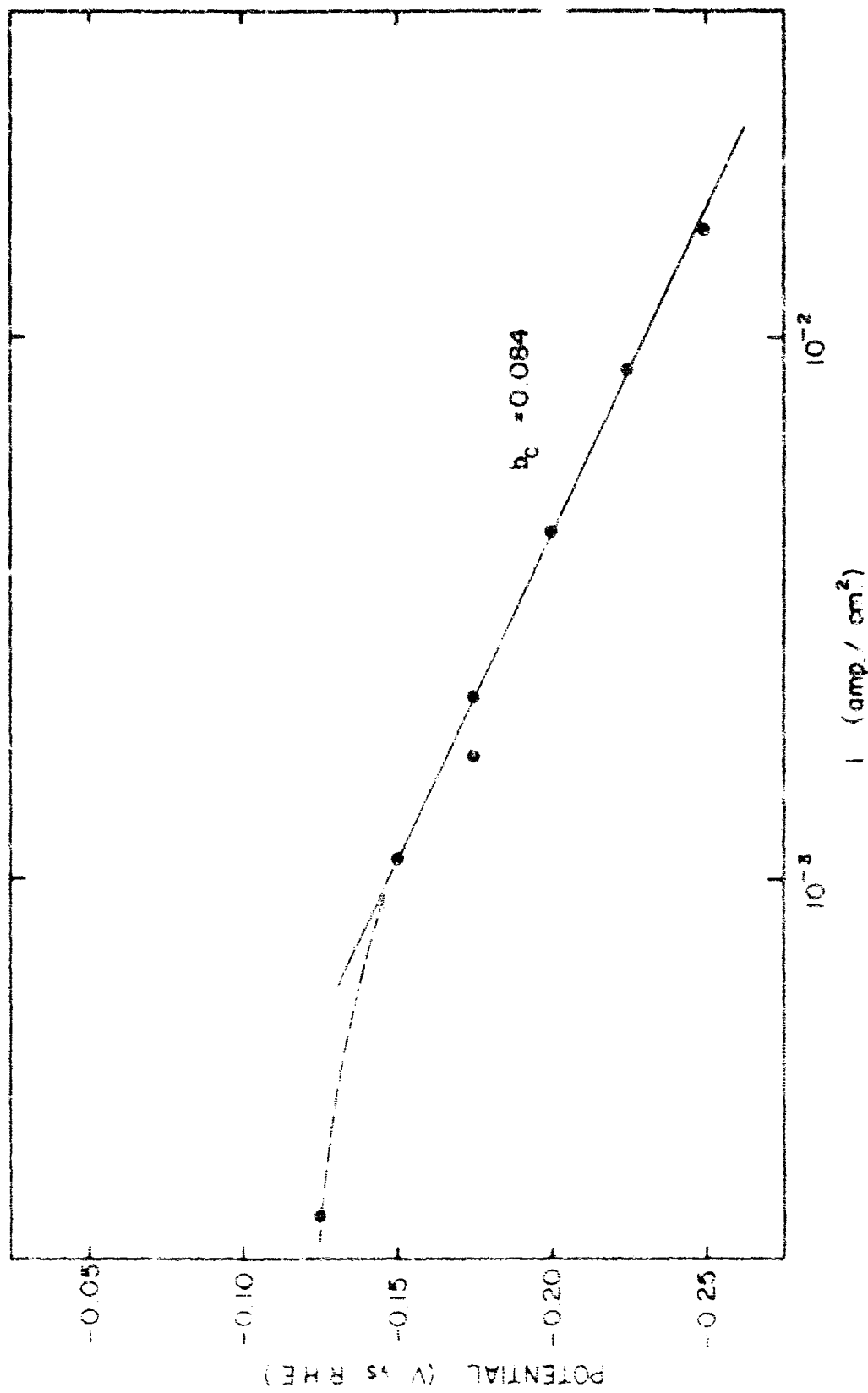


Fig. 20 Cathodic polarization curve for 80 Zn - 20 Ni in N KOH and M KCl at 30°C

III. CONCLUSIONS

Zinc alloys with Co and Ni appear promising as anodes for use in the passive, reserve mode in alkaline electrolytes.

Zinc alloys with Fe and Mn and elemental Cr and Al. and amalgamated Mg are not suitable as passivated, reserve anodes.

Addition of sulfate and chloride to KOH electrolytes does not change substantially the anodic dissolution curve of 78 Zn - 22 Co and 80 Zn - 20 Ni alloys.

IV. FUTURE WORK

Studies with mixed electrolytes will be continued using the 78 Zn - 22 Co and 80 Zn - 20 Ni alloys.

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<p>Studies of the passivation of Zn-Fe, Zn-Mn, Zn-Co, and Zn-Ni alloys were made potentiostatically. Alloys of 90 Zn - 10 Fe corrode at a high rate even when passive. Alloys of 83 Zn - 17 Mn have low, active dissolution currents. The 89 Zn - 11 Co alloys have high dissolution currents in the passive state, while the 78 Zn - 22 Co and 80 Zn - 20 Ni alloys appear promising as anodes which may be kept in a passive, reserve state. These two alloys have acceptably high critical currents and low passive currents. Their activation characteristics were studied in detail in 6N KOH; activation to about 75% of the original current density can be achieved in 20 to 90 sec, depending on the alloy and its history.</p> <p>Studies of Cr, Al, and of amalgams of Mg show them to be unsuitable for use as reserve anodes.</p> <p>Initial studies of the passivation of Zn-Co and Zn-Ni in electrolytes containing sulfate and chloride ions showed that their dissolution behavior is similar to that in KOH alone.</p>		

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14. KEY WORDS	LINK A		LINK B		LINK C	
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