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A SEMICONDUCTOR ELECTROCHEMISTRY APPROACH TO THE STUDY OF OXIDE FILMS ON NICKEL AND ZINC
Final Report

M.J. Madou, S. Wing, and M.C.H. McKubre

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Final Report

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by

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ABSTRACT

SRI continued to investigate the effect of additives to nickel and zinc battery electrodes. On nickel electrodes, we discovered the mechanisms that explain lithium and cobalt ions' contribution to improved nickel electrode performance, and we found that the cobalt might be more effective as an additive when incorporated in the plate from solution rather than in the active material beforehand. We did not find the positive effect of zincate on nickel electrodes reported by some authors; an electrical effect is thus unlikely. A structural improvement as reported by others is still possible, but the reported capacity improvement can only be confirmed on unrealistically thin battery plates. Fluoride has a negative effect on nickel electrodes (greatly reduces oxygen overpotential), and it offsets the positive effect of lithium. We found that the negative effect of zincate on the oxygen evolution can be offset to some extent by addition of LiOH, and that the positive effect of cobalt on nickel electrodes is very similar to that of lithium. We concluded that for a beneficial effect, the ions should be small (about 0.6 Å), preferably nonelectroactive, and able to act as acceptors in the NiO lattice, and that they should poison the oxygen evolution on nickel or at least not influence it. We found PbO to be a potentially beneficial additive for the nickel electrode as well. However, we determined that the PbO in this case is electroactive; to determine whether PbO is carrying more than its stoichiometric share of the current by some synergistic interaction with the NiO, we would need to perform more experiments. Magnesium has a surface catalytic effect to decrease the oxygen overpotential, which reduces the nickel electrode charge capacity (see also the effect of iron in last year's report). On zinc electrodes, iron decreases the hydrogen overpotential and should be avoided. Fluoride, which has been proposed as an additive to improve cycling of zinc electrodes, reduces the charge discharge current peaks by over a factor of ten. Zincate, which will always be present when zinc is used in an alkaline electrolyte, reduces the hydrogen overpotential at low concentrations and tends to increase it at high concentrations. Lead oxide has a beneficial effect on the zinc electrode as well and seems like a good additive for Ni/Zn batteries.

Our photocurrent experiments on the passive zinc electrode reveal the presence of an n-type semiconductor (possibly two separate phases), and impedance measurements indicate the higher resistance of the passive film on zinc in a fluoride-containing alkaline solution compared to the alkaline solution without the fluoride. More details of the impedance spectra of the passive zinc electrode could not yet be explained.

FOREWORD

Effects of additives to electrolyte and plates in a battery comprising nickel and/or zinc are well documented but not very well understood. Knowledge of the mechanism of the effect of additives, as well as the kinetics of the battery reactions, could benefit manufacturers by revealing better and cheaper additives for increasing battery performance and by suggesting different modes of plate preparation. In this work, SRI has studied half cells with cyclic voltammetry to understand the effect of additives on the separate electrodes. Nickel electrodes of different active material thickness were used to help identify bulk and surface effects of the various additives. Certain types of impedance measurements (e.g. Mott-Schottky plots) and photoeffect studies usually reserved to the study of semiconductor electrodes were performed on zinc (such measurements on nickel were reported last year) with the intention of revealing the nature of the passive films on this electrode in different electrolytes. Because of the many different additives studied, the impedance and photoeffect studies were necessarily brief, but our preliminary results are promising, and more time should be devoted to this area in the future.

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Energy Storage Division, of the U.S. Department of Energy under Contract DE-AC03-76SF00098, Subcontract 4527610, with the Lawrence Berkeley Laboratory.

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INTRODUCTION TO THE KINETICS OF THE NICKEL AND THE ZINC ELECTRODE

Nickel

It is generally accepted that cycling of a nickel electrode in alkaline solutions involves the following phases:

$$\alpha\text{-Ni(OH)}_2 \rightleftharpoons \gamma\text{-NiOOH}$$

$$\beta\text{-Ni(OH)}_2 \rightleftharpoons \text{-NiOOH}$$

The α-$Ni(OH)_2$ is unstable on standing, on open circuit, or cycling and is converted irreversibly to β-$Ni(OH)_2$. Charging the electrode converts the divalent β-phase to an oxidation state larger than +3 (γ-NiOOH or β-NiOOH). The β-phase can be more completely discharged and is thus capable of higher charging efficiency and utilization. We will see that one of the explanations for the action of some beneficial additives is that the additive prevents γ-NiOOH from forming.

Diffusion of reacting ions, primarily protons, plays an essential part in the charging/discharging of the electrode. MacArthur (1) found $DH_+ = 3.1 \times 10^{-10}$ and 4.6×10^{-11} cm^2/s for the diffusion coefficient of protons passing through the reduced and oxidized eaterial respectively. In our research last year, we performed impedance measurements on the nickel electrode to try to confirm these numbers (2).

Of particular importance in battery operation is the oxygen evolution in the charge and overcharge conditions. At standard conditions,

$$Ni(OH)_2 + OH^- = NiOOH + H_2O + e^- \qquad (1)$$

has a potential (relative to Hg/HgO) of $E_o = 0.41$ V, as compared with the oxygen evolution

$$4OH^- = O_2 + 2H_2O + 4e^- \qquad (2)$$

at $E_o = 0.307$. Fortunately for battery operation, the oxygen reaction has a higher overvoltage, which may be influenced by the presence of impurities or additives. Indeed, a beneficial additive will be shown to be one that poisons the oxygen evolution (as do lithium and cobalt cations).

Zinc

Zinc's low cost, low toxicity (relative to cadmium), and high discharge rate have made it one of the most widely used battery materials.

The discharge of the zinc negative electrodes in concentrated alkaline solutions at anodic potentials near the equilibrium value is generally agreed to proceed via the dissolution of zinc to form a complex hydroxyl zincate anion. Gerisher (3) concluded from impedance measurements that the following sequence was rate-determining in KCl supporting electrolyte:

$$Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$$

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-}$$

At high currents, electrode discharge is often terminated by the formation of a passivating ZnO layer by a dissolution-precipitation mechanism. At lower currents, rapid discharge of the zinc electrode is associated largely with the solubility of Zn(II) as a zincate ion. However, high zincate solubility limits the cycle life of the zinc electrodes in an electrochemical rechargeable cell, permitting the zinc to be deposited in a dentritic or nonadherent form during charging, and allowing the electrode to change shape with cycling. Considerable effort has recently been reported to reduce the solubility of the zinc in the solution in order to overcome the shape change problem. Additives that reduce the hydrogen evolution could also improve the energy efficiency of the battery plate. Amalgamation of the zinc is an obvious, but expensive, means of accomplishing this reduction.

Apparatus and methods (cell, electrode, electrolytes, and electrode surface pretreatment), as well as methods for making thick NiO films, were discussed in last year's report (2) and will not be repeated here. The zinc electrodes used in this study were high-purity zinc discs embedded in an epoxy holder at the end of a L-shaped glass tube and polished flat with the epoxy head; further contacting was done through a lead on the back of the zinc disc and through the glass tube.

EFFECT OF ADDITIVES ON THE NICKEL AND ZINC ELECTRODES

Background

Additives to the electrode and to the electrolyte, whether intentionally or unintentionally introduced, can have a major influence on battery behavior. In the case of nickel, the influence of various additives to the electrolyte have been studied quite extensively. Weiniger (4) recently charted additives to the $Ni(OH)_2$ electrode that have been studied since 1958, as shown in Figure 1. The elements without circles or squares were studied before 1965. The circled elements--beryllium, silicon, and lead--were studied by Harviel and coworkers (5). Selenium was studied by D. Crispis (6). The most extensive research efforts have concentrated on the few elements that have proven to better the performance of the NiOOH: cobalt and lithium, and, to some extent, zinc, in the form of ZnO. (With respect to ZnO there is some controversy; some authors have ascribed deleterious effects to this additive, other say it has a beneficial effect.) The process by which these additives work is very little understood, especially in the case of the additives that have a positive influence on battery performance. In the case of cobalt, for example, understanding the details of its function might allow manufacturers to use cheaper substitutes. [In the USSR, barium is used as a substitute, for example (7).]

	I	II	III	IV	V	VI	VII	VIII
2	Li	(Be)	B					
3	Na	Mg	Al	(Si)				
4	K / Cu	Zn	Sc		As	Cr / [Se]	Mn	Fe Co
5	Rb / Ag	Cd		Sn	Sb	Mo		
6	Cs	Ba / Hg	RARE EARTH	(Pb)	Bi	W		

SOURCE: Ref. (4)

FIGURE 1 TESTS OF ADDITIVES TO $Ni(OH_2)$ REPORTED IN THE LITERATURE

In the case of zinc electrodes, the main interest for many years has been to reduce the solubility of the zincate in the electrolyte, with the aim of improving the life of zinc-based batteries. In this context, SRI investigated the effect of F^-, which reduces the solubility of zinc, on zinc electrode behavior. Another goal for zinc electrodes is to reduce hydrogen evolution, which could increase charge capacity. Amalgamation is a rather obvious but costly technique: finding alternatives by adding some hydrogen poisons that do not otherwise affect the battery would be the real solution.

One of the difficulties with electrodes is that during charging, the voltages for hydrogen evolution and iron reduction are similar. This hydrogen gas reaction causes inefficiency in the charging of the iron electrode. O'Connel reported (8) that the addition of small amounts of sulfur-bearing anions to the electrolyte, for example, reduces the hydrogen evolution, and an understanding of the underlying phenomena would help battery design. However, because of time constraints, we have not been able to do significant work on the iron electrode this year.

By performing cyclic voltammetry and impedance measurements in the presence and the absence of various additives on single electrodes, we have been able to simplify the assignments of known battery phenomena to either one of the half cells. Furthermore, by comparing cyclic voltammograms of electroactive material of different thicknesses (especially nickel) we were able to distinguish between bulk and surface effects. For example, if the influence of additives on $Ni(OH)_2$ is surface specific, then the additive effect should be enhanced by use of a thin film electrode rather than structures in which bulk properties are more pronounced. In the case of $Ni(OH)_2$ we also tried to incorporate some of the impurities in the film. These techniques were used quite extensively by Weiniger (4).

In general, we believe that our results could benefit battery manufacturing but caution is required when extrapolating our data from single electrodes (which in general have only limited amounts of active material) to commercial cell design.*

Nickel

Many of the experiments on nickel were described in the previous report (2). We have repeated some of the experiments this year and conducted new experiments. The complete list of additives tested on NiO is

---

*A Hg/HgO electrode was used as the reference electrode for the study of additives on the nickel electrode and zinc electrode behavior. The potentials were not converted to the Standard Hydrogen Electrode (SHE) in the figures as in many cases the exact conversion factor for the specific solutions used is not known exactly.

shown in Table 1. The additives shown with an asterisk were studied last year; the others were studied last year but may also have been tested again this year. Procedure C-type film mentioned in Table 1 was made by electrodeposition from 0.1 N $NiSO_4$, 0.1 N NaAc, and 0.001 N KOH in water on a nickel metal electrode. The film has a charge capacity of about 62 mC/cm^2 and was used to emphasize bulk effects (as compared to the bare nickel electrode or the single crystal NiO electrode).

Table 1

TEST OF ADDITIVES TO VARIOUS TYPES OF NiO ELECTRODES

Additive	Bare Nickel Electrode	NiO		
		Single Crystal	(C-film)	Impurity Incorporated
KOH (21% or 18.1%)	x	x	x	x
Li	x	x	x	x
Co	x	x	x	x
Fe	x	x	x	x
Ba	x	x	x	x
Ni	x	x	x	x
Mg*	x	x	x	x
F^-*	x	x	x	x
Zincate*	x	x	x	x
PbO (30% KOH 2% in)*	x	x	x	x

*Studied this year

Lithium

One of the additives studied on nickel last year (and again more this year) is lithium. We feel that we now have a somewhat better understanding of the Li^+ effect. The beneficial effect of lithium hydroxide on the nickel oxide electrode was discovered by Thomas Edison (9). Since that time, lithium hydroxide has been a standard ingredient in the potassium hydroxide electrolyte in nickel-iron cells. It is also used in nickel-cadmium cells, although not to the same extent. In the nickel-iron cells, LiOH has a favorable effect on the capacity and on the life of the positive electrode. In the Ni-Cd cell, lithium's effect

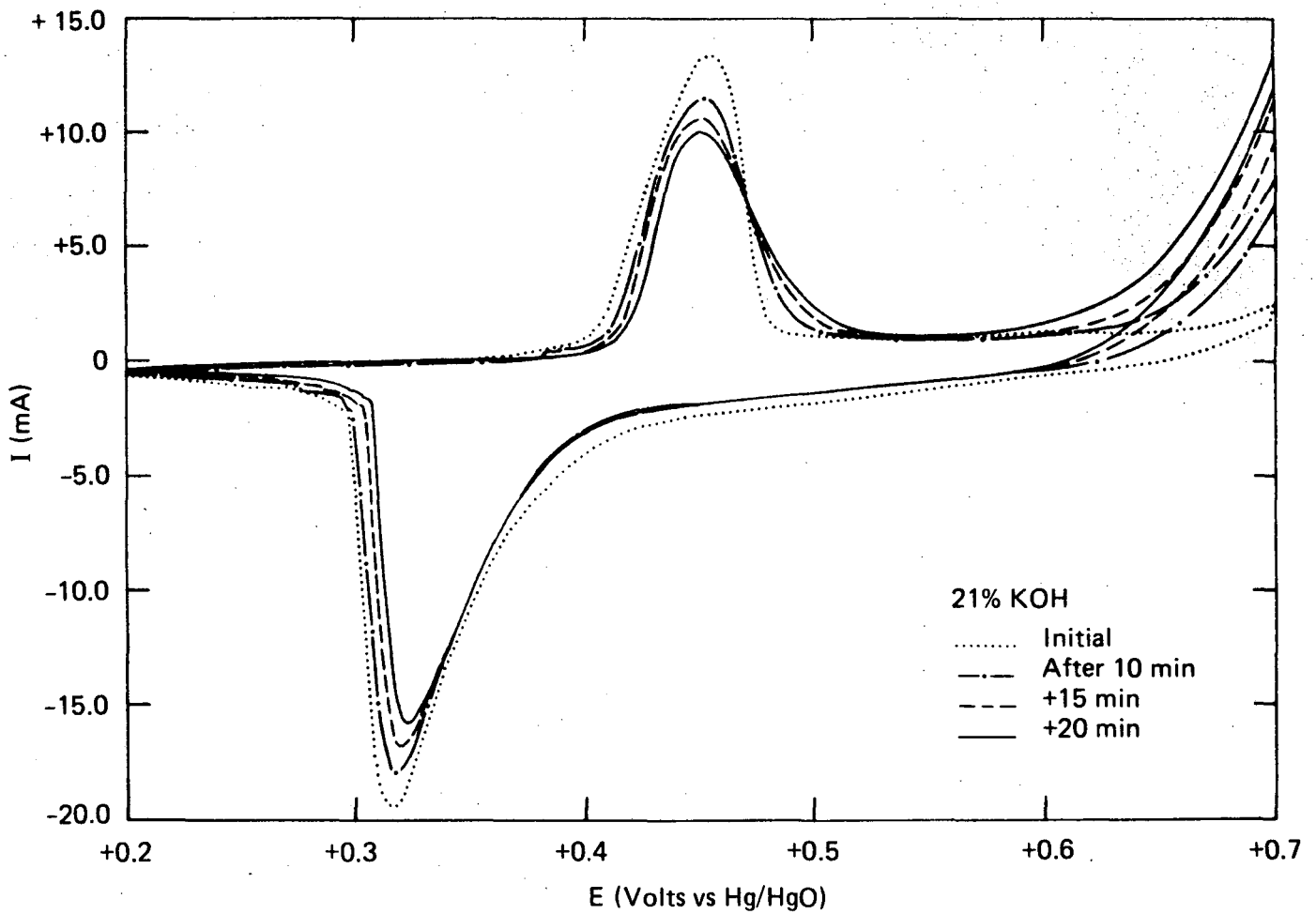
on capacity is very limited, but its effect on life is pronounced. Lithium is said also to be beneficial on the zinc electrode in Ni-Zn cells in stabilizing the capacity on cycling (10). [Results of lithium addition to a zinc electrode will be discussed under the heading "Zinc". The combined effect of lithium cations and zincate anions on a nickel electrode will be discussed when describing the zincate effect on nickel.]

Explanations given for the positive effect of LiOH are diverse. We have disproven some of the older explanations and can now support some of the more recently advanced theories: donor compensation by the acceptor lithium leads to an electronically more resistive film, which increases the oxygen overpotential (see below).

The effect of lithium additions to the alkaline electrolyte (21% KOH) on the electrode is illustrated in the series of voltammograms shown in Figure 2. Figure 2(a) can be considered the reference voltammogram. When the nickel electrode is held in a 21% KOH solution at 0.2 V vs. Hg/HgO for various times (0, 10, 15, and 20 minutes), a marked increase in the oxygen evolution as a function of lapsed time is always noticed with both the bare nickel electrodes (which are nickel electrodes without intentionally grown oxide) and C-type NiO films; the effect is much less pronounced for single crystal NiO. This effect has been named by some authors the "aging effect of the NiO." Figure 2(a) illustrates this effect for a bare nickel electrode. When repeating the same experiment with the same timing but with various amounts of LiOH added to the KOH, as shown in Figures 2(b), (c), and (d) for bare nickel electrodes and C- type films, we notice that:

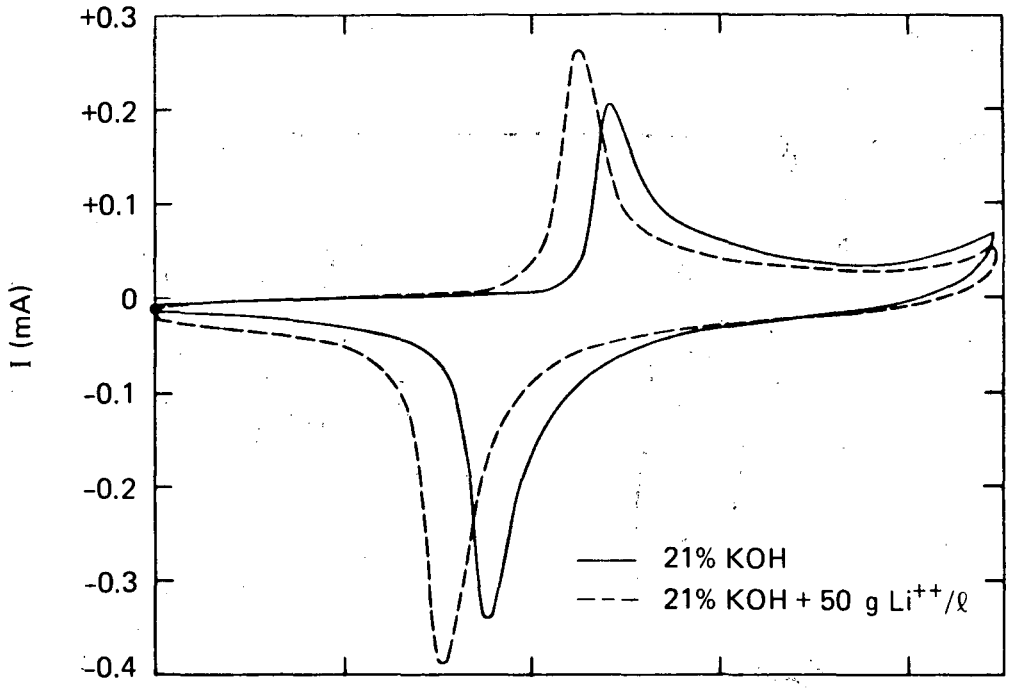
- The absolute oxygen evolution rate is much smaller.
- The so-called "aging effect of the NiO" is delayed.
- In all cases the charge/discharge rates do shift cathodically (less overpotential), but the amount of charge under the peaks increases markedly only in the case of the bare nickel electrode; in the other cases, the charge actually decreases.

The influence of lithium on the cyclic voltammogram on a single crystal is shown in Figure 2(e). Although the phenomena on the single crystal are very poorly resolved, it seems that the influence of the lithium addition is very small compared to, for example, the influence on the bare electrode. We found that to dope single crystal NiO (in order to make it p-type with lithium as the acceptor) we had to use temperatures as high as 1500°C and anneal for extended periods, ~30 hours, to dope a layer only 100-μm thick. It seems logical to assume that no lithium ions can penetrate the lattice at room temperature, which indicates that the lithium effect (which is almost completely absent in the case of the single crystal, but pronounced on the bare electrode with its more open and penetrable nickel hydroxide layer) is a bulk effect, rather than a surface catalytic effect. All the beneficial effects of the lithium on the bare nickel electrode were also observed for the C-type films, except the increase in charge capacity. However, ours was a

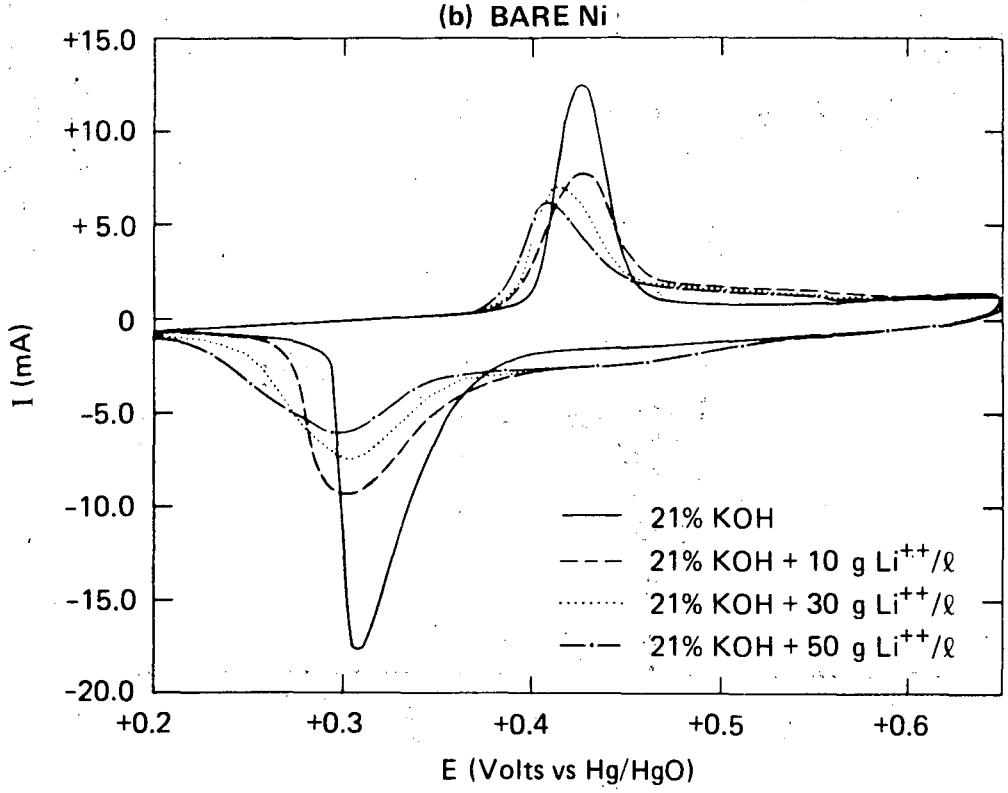


(a) C-TYPE NiO FILM

FIGURE 2 EFFECT OVER TIME OF LITHIUM ADDITIVE ON CYCLIC VOLTAMMOGRAMS, 50 mV s^{-1}, ALKALINE ELECTROLYTE

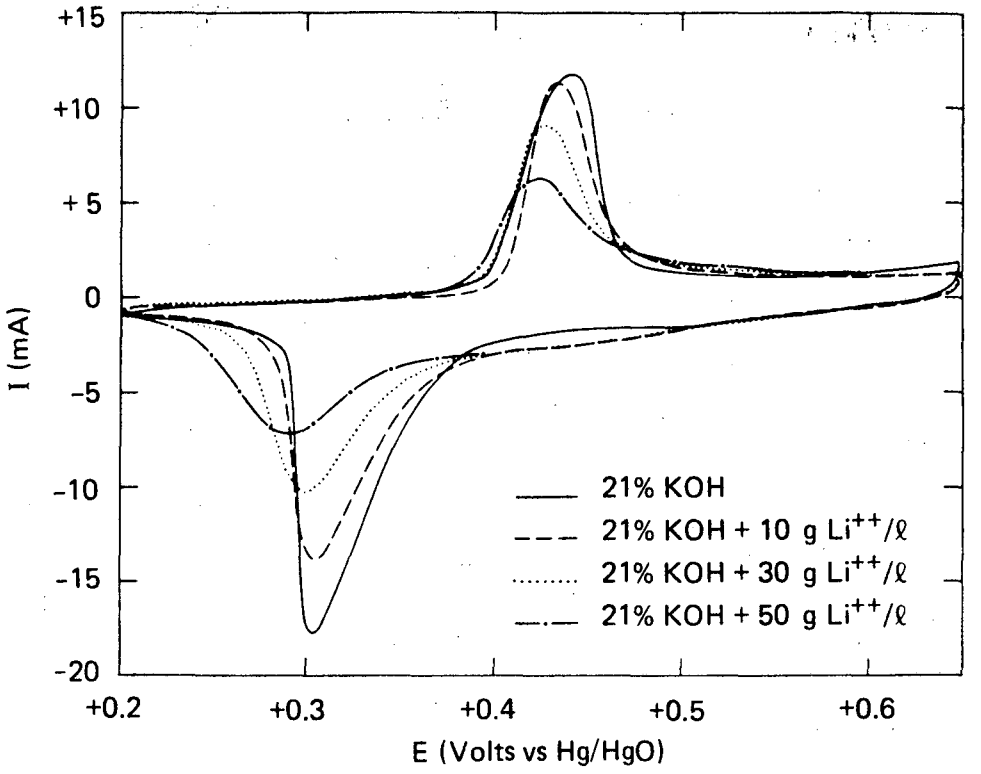


(b) BARE Ni

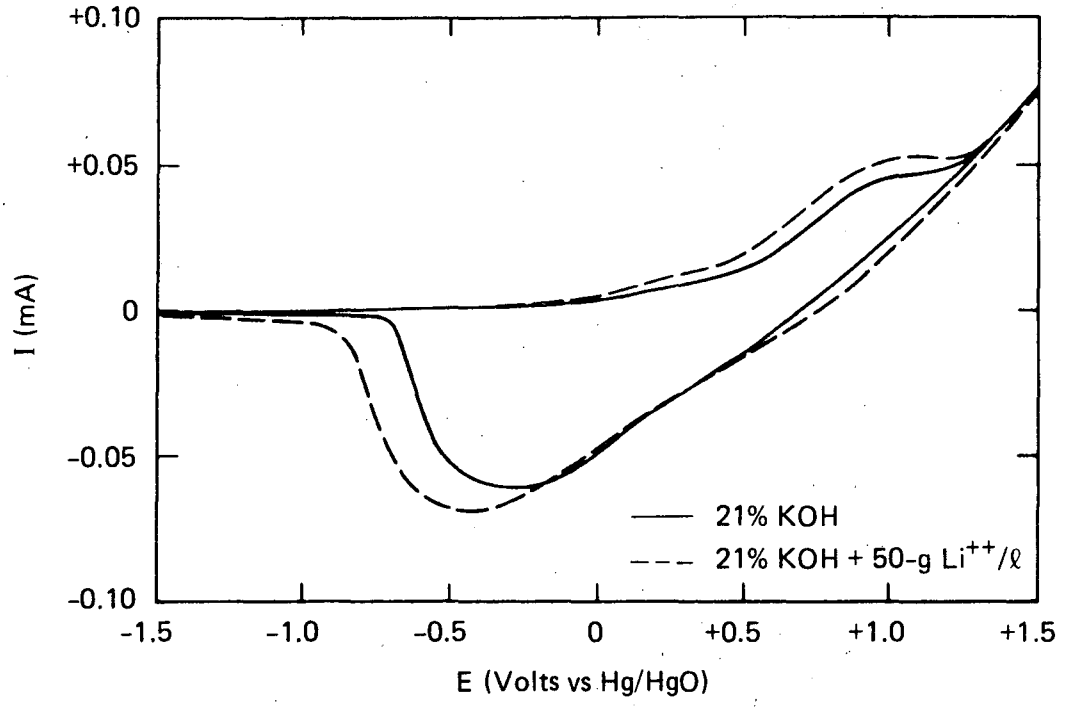


(c) NiO (C-FILM)

FIGURE 2 EFFECT OVER TIME OF LITHIUM ADDITIVE ON CYCLIC VOLTAMMOGRAMS, 50 mV s^{-1}, ALKALINE ELECTROLYTE (Continued)



(d) NiO (Li^{++} INCORPORATED C-FILM)



(e) NiO SINGLE CRYSTAL

FIGURE 2 EFFECT OVER TIME OF LITHIUM ADDITIVE ON CYCLIC VOLTAMMOGRAMS, 50 mV s^{-1}, ALKALINE ELECTROLYTE (Concluded)

dynamic experiment (the sweep used was 50 mV/s) and the increased capacity seen on real battery plates in the presence of lithium is measured in quasi-static experiments.

Earlier researchers (11) assumed that Li^+ increased the p-type conductivity of the p-type nickel oxide material, thus improving battery operation. Because Li^+ is a known acceptor in NiO, this theory seemed plausible at first, but we have conducted two experiments to discredit it. We found that the doping level of thin films of hydrous nickel oxide material, as determined from Mott-Schottky plots in the discharge potential range [see Ref. (2)], did not increase when the electrode was measured in a solution containing LiOH. So, although lithium cations probably penetrate the hydrous nickel material, they do not of themselves alter the electronic properties of this material in the electrode discharge region. We also found that the changes in the cyclic voltammograms in the presence of lithium occur in the potential region of charging of the nickel oxide; we determined by observing the sign of the photoeffect [see Ref. (2)] that the oxide behaves as an n-type rather than a p-type. We propose, as some authors have done independently but previous to the current work (12), that the lithium compensates the donors in that oxide and makes the oxide more electronically resistive, thereby explaining the observed increase in oxygen overpotential. All our experiments seem to confirm this theory. Our experiments do not exclude Weiniger's (4) idea that Li^+ prevents K^+ from entering the lattice, thereby also increasing the overpotential for oxygen. The β-phase can be discharged more completely than the γ-phase and thus gives rise to higher charging efficiency and utilization. This is attributed to the greater involvement of K^+ ions in the γ-phase. Since Li^+ prevents K^+ ions from entering the lattice, the β-phase will be favored and this results also in an increase in oxygen overvoltage, because the recombination of absorbed oxygen is hindered allowing greater charge acceptance.

If lithium is incorporated in the nickel oxide film by electrodeposition from a solution containing LiOH [Figure 2(d)] one gets the same behavior as with the Li^+ in solution; this result suggests that Li^+ from solution is quickly incorporated in the NiO film, so that the two situations produce the same result.

Zincate and Combined Zincate/Lithium/Fluoride Effect

Zincate. Besides lithia, zinc oxide is probably the most important additive in alkaline batteries. (It is used in silver-zinc and nickel-zinc cells.) In nickel-zinc cells, zincate has been reported to have a poisoning effect on the nickel oxide electrode. According to Flerov (13), up to 30% of electrode capacity can be lost because of the ZnO presence on a pocket-type positive electrode; up to 80% in a sintered type. The zincate ion is an unavoidable ingredient: although it has essentially negative effects on the electrical performance, Falk and Salkind (13) claim that it has beneficial effects on the charge retention.

Not all authors agree that zincate has negative effects. Weiniger (4) finds that Zn^{2+} (like Co^{2+}) improves capacity and cycle life. Fritts (14) found that zinc hydroxide is beneficial to the nickel oxide electrode; more specifically, he found that coprecipitating zinc hydroxide with nickel hydroxide can provide a more dimensionally stable electrode, but with some slight loss in electrode utilization efficiency.

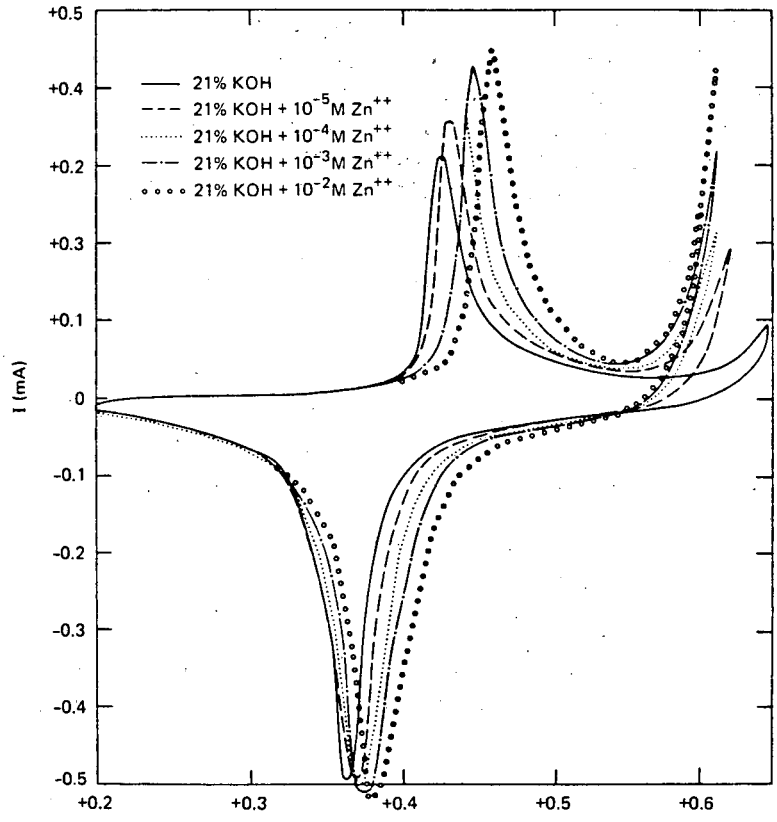
Because of these seemingly controversial findings, SRI conducted a more fundamental study. The effect of zinc on nickel hydroxide behavior is illustrated in Figure 3. Adding zinc increases the oxygen evolution rate in the case of the bare electrode [Figure 3 (a)]. Furthermore, both charge and discharge peaks moved toward more anodic potentials with increasing zinc concentration. However, the peak height increased with increasing zinc concentration, which tends to support Weiniger's contention (4) that there is a charge capacity increase due to zinc. In the case of the C-type film (with zinc added to the solution), the peaks do shift towards more anodic potentials, but the oxygen evolution rate and peak height are not greatly changed. Incorporating zinc within the film seems to have less effect than having zincate in solution [compare current levels in Figure 3(b) and 3(c)]. Weiniger (4) concluded that adding foreign ions into the lattice from the electrolyte is more effective than direct incorporation by co-precipitation, co-deposition, or alloy oxidation.

Results with the single crystal are like those with the bare nickel electrode except that the peaks do not shift.

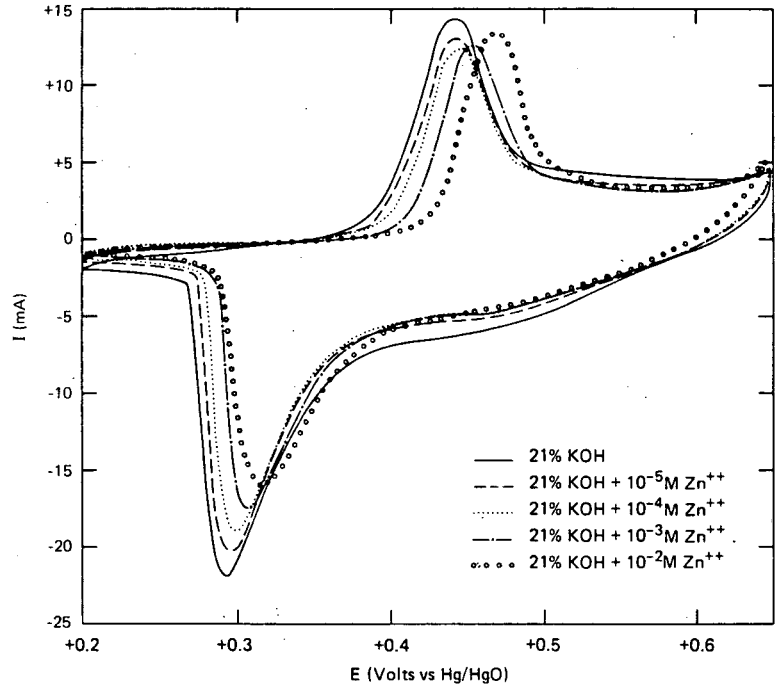
The effect of zinc on the oxygen evolution rate seems to be a surface effect (it is most pronounced with the thinnest films), and in more realistic structures where the bulk properties should dominate (as in the C-type film), the oxygen effect seems to be minor. The shift in the potentials should still lead to a negative overall effect on the electrical characteristics [as claimed on data on thin films and as shown in our Figure 3(a), where one can indeed see more charge underneath the anodic and cathodic peaks]; but because these are dynamic measurements, they do not necessarily translate to an improved battery plate charge capacity. Our measurements are not sophisticated enough to confirm Fritts' (14) observation that zinc in the nickel plate provides to an improved electrode structure but with a slightly reduced charge capacity.

In conclusion, loss of efficiency due to increased oxygen evolution might be of little importance, because with thick plates surface phenomena will be relatively unimportant. The main effect of adding zincate on a nickel electrode would thus seem to be a structural improvement rather than an electrical effect. Perceived capacity increases can be confirmed only on unrealistically thin battery plates.

<u>Zincate/Lithium/Fluoride</u>. F^- ions suppress the solubility of the zinc in a Ni/Zn battery (see discussion under "Zinc" for the effect of fluoride on zinc), and it is important to know how this reduced solubility would affect the nickel electrode. At the same time we might want

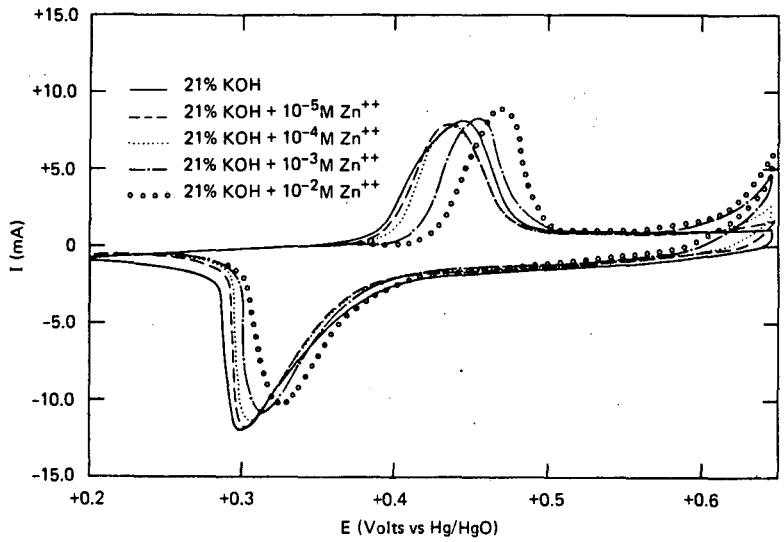


(a) BARE Ni

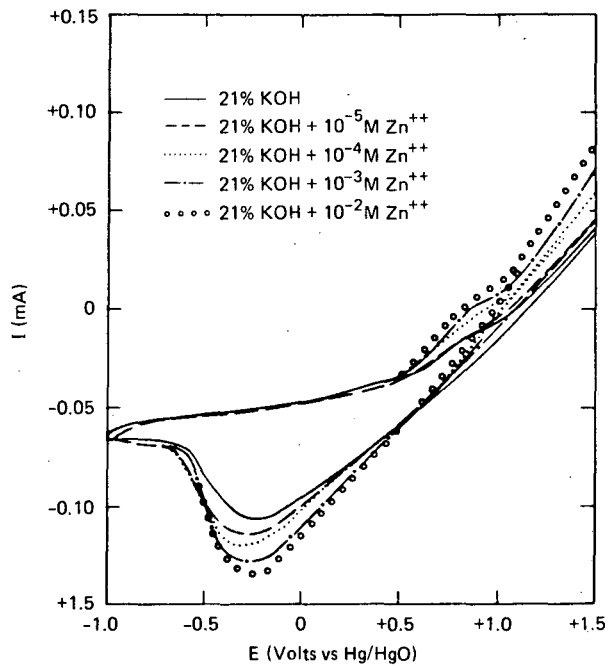


(b) NiO (C-FILM)

FIGURE 3 EFFECT OF ZINC ADDITIVE ON CYCLIC VOLTAMMOGRAMS, 50 mV s^{-1}



(c) NiO (Zn++ INCORPORATED C-FILM)



(d) NiO (SINGLE CRYSTAL)

FIGURE 3 EFFECT OF ZINC ADDITIVE ON CYCLIC VOLTAMMOGRAMS, 50 mV s^{-1} (Concluded)

to improve on the nickel electrode behavior itself by adding fluoride. Dissolved zincate will be unavoidable in this cell, so we have an opportunity to study the combined effect of these impurities on the nickel electrode. SRI's results on a bare nickel electrode are shown in Figure 4. The solutions in the legend marked LBL (15% KOH, 1% LiOH, saturated ZnO and 15% KOH, 1% KF, saturated LiOH, saturated ZnO) are currently used at LBL in the study on the cycle-life of zinc electrodes. (Experimental results on behavior of zinc electrodes in these solutions is presented later.)

The obvious difference in the cyclic voltammograms measured on nickel in the two "LBL" solutions is that in the presence of fluoride the oxygen evolution rate is drastically increased in the same potential range. The presence of fluoride thus offsets the beneficial effect lithium has on the oxygen overpotential. Comparing the cyclic voltammogram in the second "LBL" solution with the one in the 15% KOH, saturated LiOH, saturated ZnO (the only difference being the presence of KF in the "LBL" solution), it is clear that fluoride also counteracts the other characteristic of lithium presence: the cathodic shift of the charge/discharge peaks. The cyclic voltammogram in the solution of 15% KOH and 15% KF exhibits copious oxygen evolution, illustrating again the deleterious effect of the fluoride on the oxygen overpotential; moreover, it shows that fluoride, as with zincate addition, causes the charge and discharge peaks to shift anodically. Nevertheless, the presence of LiOH can offset the deleterious effect of the presence of dissolved ZnO on the oxygen overpotential [see Figure 3(a)]. In the solution 15% KOH, 1% LiOH, the peaks are shifted cathodically, as expected [see also Figure 2(b)].

Judging from the cyclic voltammograms measured in 15% KOH, 1% LiOH, and saturated ZnO and in 15% KOH, saturated LiOH and saturated ZnO, the peak position can be shifted by changing the LiOH/ZnO ratio; the higher this ratio the further the peaks shift cathodically, while maintaining a large overpotential for oxygen. We conclude from the above experiments that fluoride not only has a negative effect on the nickel electrode but that it offsets the positive effect of lithium addition. We can conclude also that zincate's negative effect on the oxygen evolution and a shift toward anodic potentials can be offset to some extent by the addition of LiOH.

Cobalt

As an additive for the nickel electrode in Ni-Cd storage batteries, cobalt can be used to improve the charge efficiency of the electrode and the utilization of the active material, and to stabilize the capacity of the Ni-Cd batteries during cycling. It is claimed that the presence of Co^{3+} in the lattice prevents the γ-NiOOH phase from forming in favor of β-NiOOH formation. The β-NiOOH can be more completely discharged than the γ-NiOOH and thus yields higher charging efficiency and utilization. (The tighter incorporation of K^+ in the γ-phase supposedly hinders the complete reduction to $Ni(OH)_2$. It is also important to note that Co^{3+} is neither ordered nor reduced with electrode cycling.) We will further

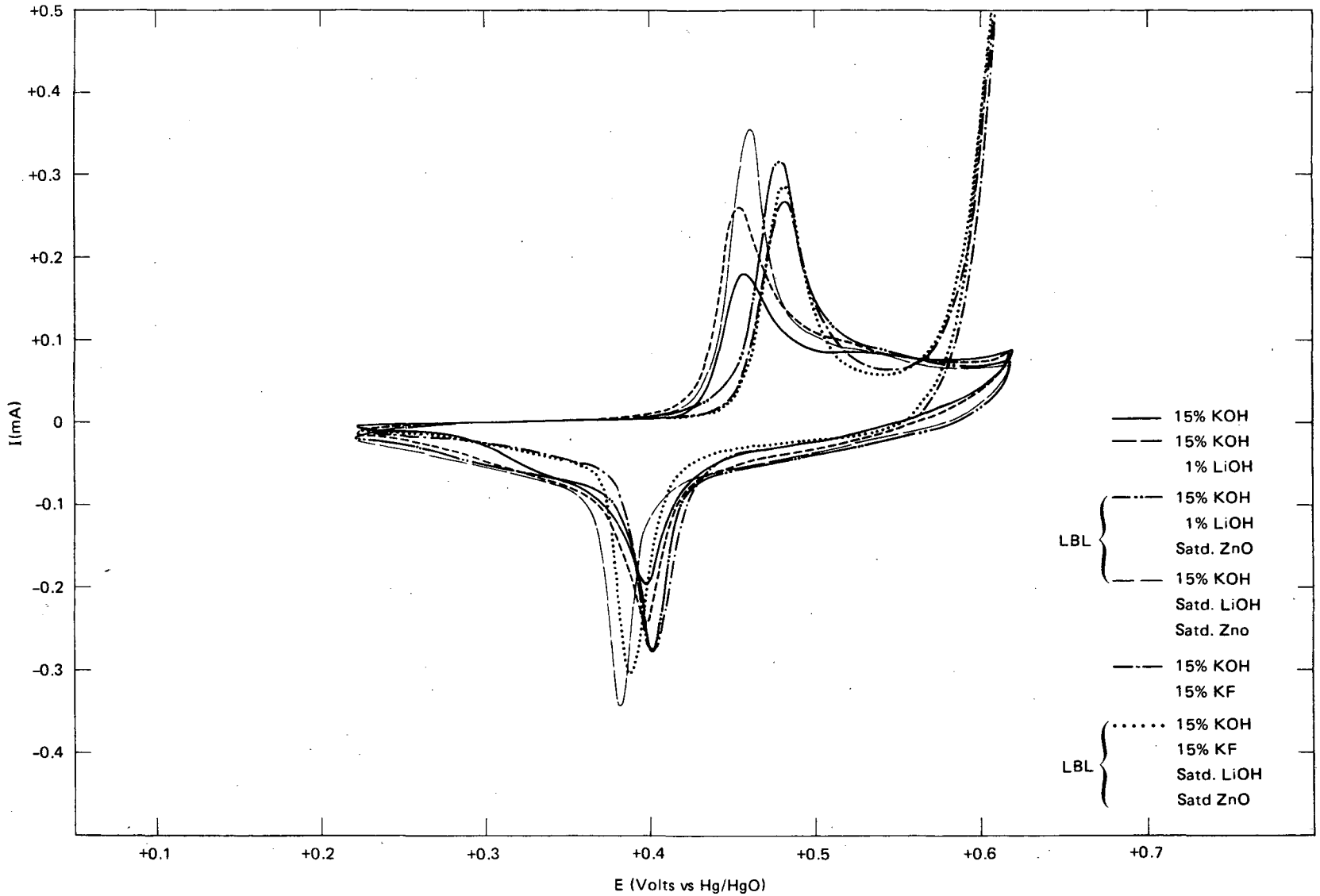


FIGURE 4 EFFECT OF FLUORIDE ADDITIVE ON CYCLIC VOLTAMMOGRAM, BARE NICKEL ELECTRODE, 50 mV s^{-1}, AREA = 0.196 cm^2

see that another additive that is potentially beneficial to the nickel electrode, PbO, does change oxidation state while cycling the nickel electrode. The explanation that Weiniger (4) gives for the cobalt effect is basically the same as the explanation given for the lithium effect. Both arguments are based on incorporating these additives in the nickel hydroxide lattice and preventing the tight incorporation of K^+. The size of Li^+ is 0.6 Å and that of Co^{3+} is less than 0.74 Å, while the K^+ radius is 1.33 Å (unhydrated ions); the idea of the cobalt and lithium ions preventing the potassium ions from entering the lattice is thus quite feasible.

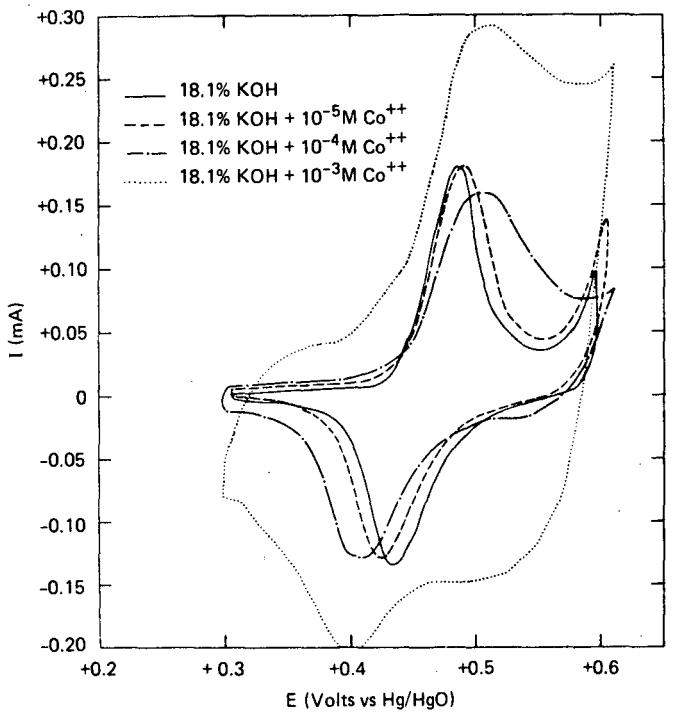
The experiments in Figure 5(a-d) illustrate the cobalt effect. Figure 5(a) shows a dramatic increase in capacity at concentrations of 10^{-4} M of cobalt ions; this is also the point where precipitation on the electrode occurs. There is also much more current in the range between charging and the onset of the oxygen evolution in the presence of cobalt. We think the cobalt is not active when it is dissolved in the solution; it affects the nickel only when contained within the electroactive material. For the C-type film there is also an increase in electrode capacity observed, especially in the range between charging and the onset of the oxygen evolution [Figure 5(b)]. Incorporating the cobalt in the electrodeposited film has little additional effect [Figure 5(c)], and the effect of cobalt addition on a single crystal is minor (Figure 5d).

Like the results obtained for lithium, these results indicate that the cobalt effect is a bulk effect and that the cobalt ions can move quickly into the nickel oxide. The aging effect is also delayed, which reinforces the idea that both additives act in a similar fashion to improve the behavior of the nickel oxide electrode. To replace the cobalt and lithium additives, we should thus study cations that can easily be incorporated into the lattice of the nickel hydroxide and are not catalysts for the oxygen evolution reaction.* The ions of choice should be small (0.6 Å or less); they should be poisons for the oxygen reaction or at least not influence it; they should preferably be non-electroactive; and, according to the theory we have proposed to explain the effect of lithium, they should also be able to act as acceptors in the NiO lattice. In next year's program, we propose to explore attractive candidates to replace cobalt on the basis of the above recipe.

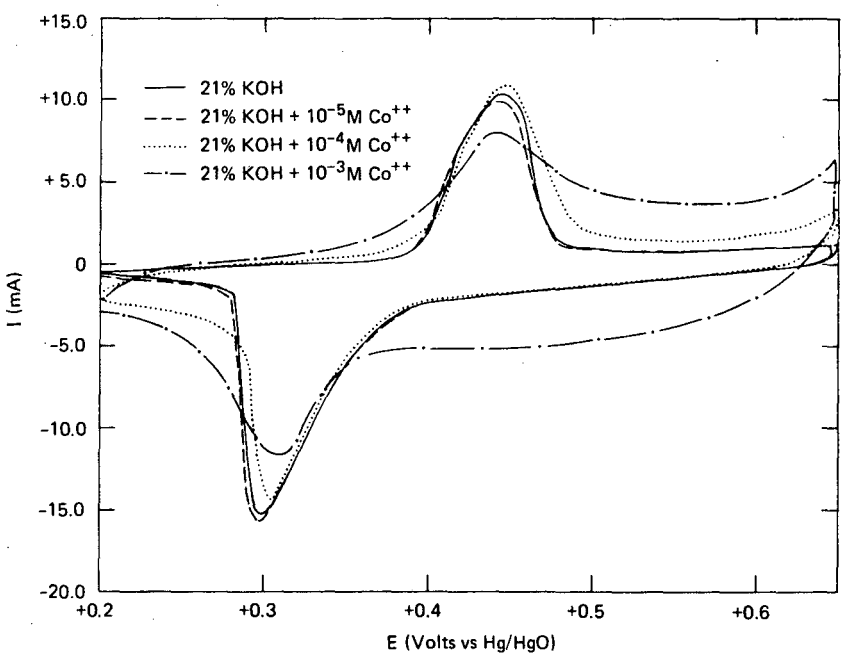
Lead Oxide

There has been little work reported on the effect of adding lead to a nickel electrode. We found that adding 2% PbO to the alkaline electrolyte had a very pronounced effect on the nickel electrode. Figure 6

*For both lithium or cobalt, it does not seem to make a difference if they are added to the electrolyte or if they are incorporated in the electrode plate. We believe that the cobalt is actually more effective to add to the electrolyte. [This is also the opinion of Weiniger (4).]

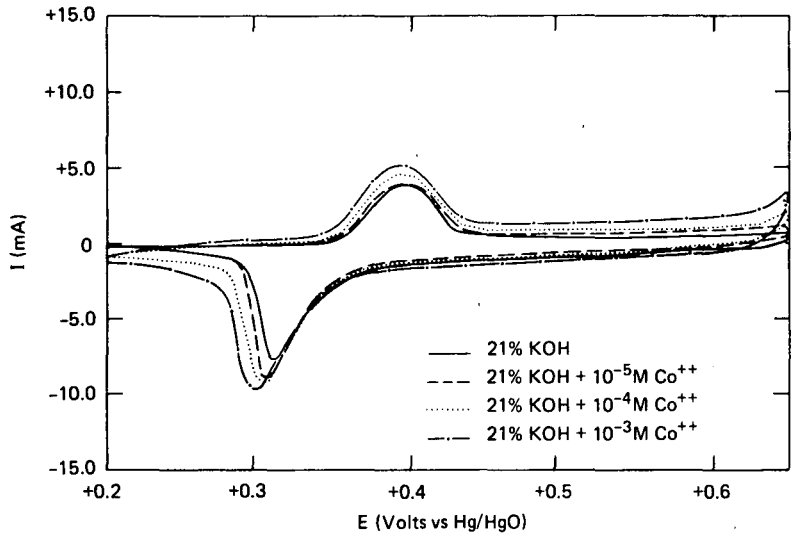


(a) BARE Ni

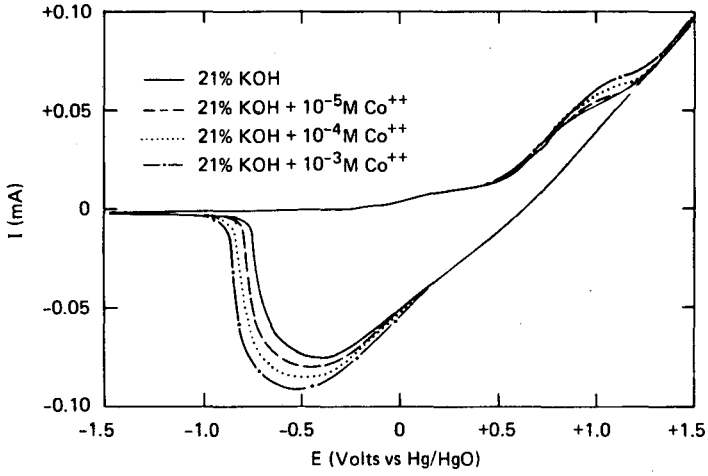


(b) NiO (C-FILM)

FIGURE 5 EFFECT OF COBALT ADDITIVE ON CYCLIC VOLTAMMOGRAMS, 50 mV s^{-1}



(c) NiO Co^{++} INCORPORATED C-FILM)



(d) NiO (SINGLE CRYSTAL)

FIGURE 5 EFFECT OF COBALT ADDITIVE ON CYCLIC VOLTAMMOGRAMS, 50 mV s^{-1} (Concluded)

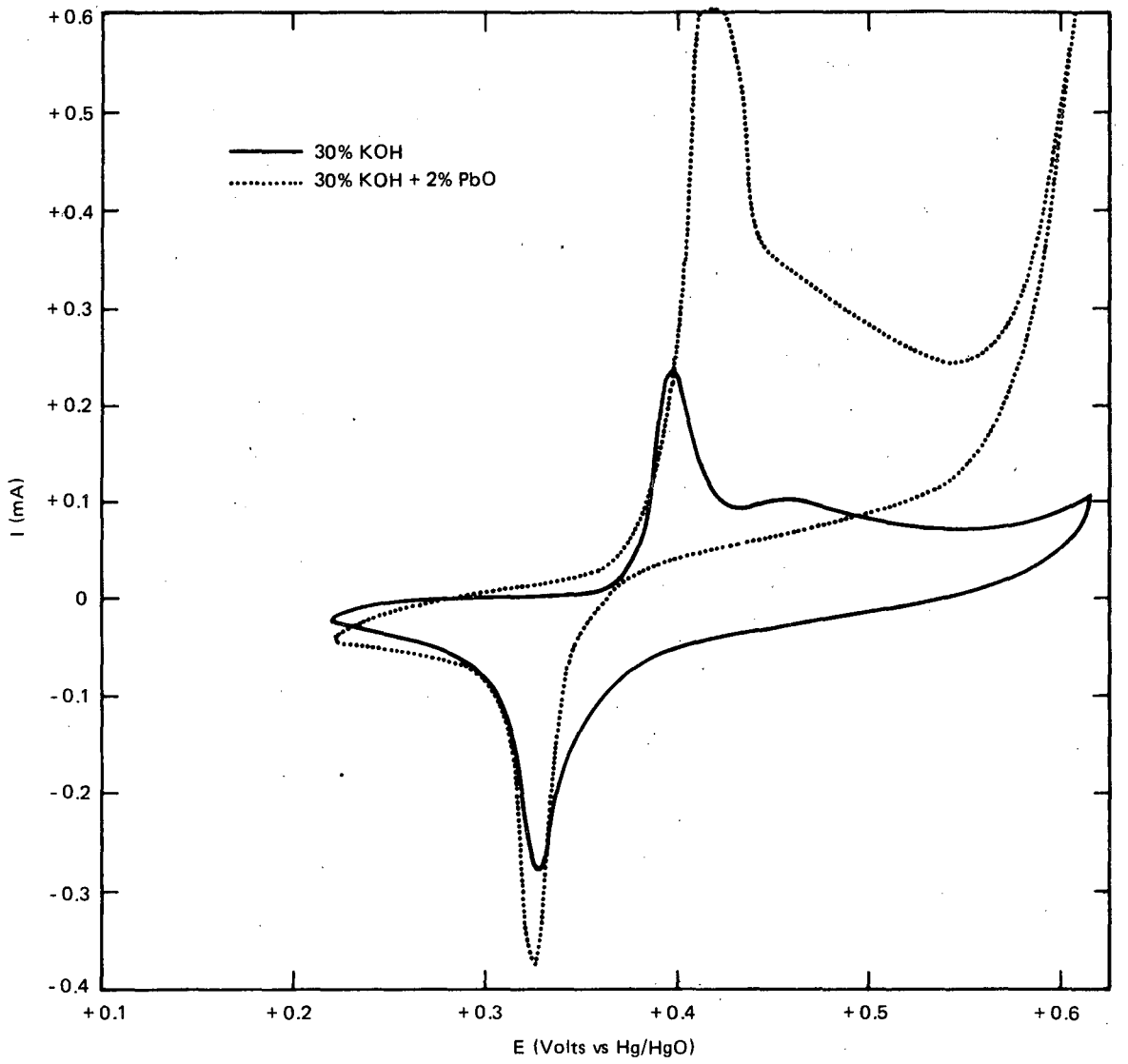


FIGURE 6 EFFECT OF LEAD ADDITIVES ON CYCLIC VOLTAMMOGRAMS, BARE NICKEL ELECTRODE, 50 mV s^{-1}, AREA = 0.15 cm^2

shows that when 2% PbO was added to the electrolyte, there was a large increase in currents, both anodic and cathodic, compared to the cyclic voltammogram on nickel in the 30% KOH solution. These results indicate that adding PbO will mean improved charge capacity for the nickel electrode in a battery, and PbO thus seems to have the potential for the same beneficial effect on battery performance as the cobalt addition. However, the cyclic voltammograms, although indicating much more charge, are highly asymmetrical. The amount of current increase under the anodic peak is much larger than that under the cathodic peak. (Only one cyclic voltammogram is shown in Figure 6 but in subsequent cyclic voltammograms the same holds true.)

Figure 7 shows cyclic voltammograms on a platinum electrode in a 30 % KOH/2% PbO solution and a 30% KOH/1% LiOH/saturated ZnO. (The same Hg/HgO reference electrode was used as for the nickel work.) Clearly in the case of the PbO containing solution there are redox reactions occurring in the potential range of NiO charging. The current associated with the oxidation reactions of the PbO can thus add to the current associated with the nickel oxide oxidation reaction. In the nickel oxide discharging potential range covered in Figure 6, there is little corresponding PbO reduction reaction current to add to the nickel oxide reduction current, and therefore the currents in this potential range are barely larger than without the addition of the PbO. From Figure 7 it is clear that the reduction of the PbO occurs quickly and effectively only in the potential range negative of 0 V vs Hg/HgO. The lead oxide redox system in this medium obviously represents a less reversible system than the nickel oxide; some of the oxidation reactions coincide, but the reduction reactions are displaced with respect to each other.

To construct the above argument we have assumed that the redox reaction of lead oxide occurs on platinum and nickel at the same potentials. We believe this to be a reasonable assumption. By polarizing the nickel electrode to more negative potentials, or leaving it longer at open circuit, the PbO is reduced, and in subsequent cycles more PbO oxidation reaction is again possible. The above explains the asymmetry in the cyclic voltammograms in Figure 6. A battery usually will not be charged/discharged at the rates we used to take our data, so the effect of PbO could still be beneficial. Indeed, although the PbO clearly is electroactive (unlike the cobalt, see above) it could carry more than its stoichiometric share of the currents because of some synergistic effect between the nickel oxide and the lead oxide C-type films, and possibly even more on plates of commercial thicknesses containing more active nickel oxide material. A detailed investigation of this phenomenon is one of the tasks we have set for next year's work.

Magnesium

Magnesium ions are reported to have a detrimental effect on the capacity of the nickel hydroxide electrode (11). The effect of magnesium on the bare nickel electrode and single crystal NiO is illustrated in Figure 8(a) and (b). The concentration of magnesium added to the alkaline solution was varied between 10^{-5}M Mg^{++} and 10^{-2}M Mg^{++}. On the bare nickel electrode, we observed that the oxygen evolution increases with increasing Mg^{++} concentration; this is also the case on the single crystal NiO. The rather large effect of magnesium on the oxygen evolution on the single crystal suggests that we are dealing with a surface effect.

In the case of the bare nickel electrode, both the charging and discharging peaks moved toward more anodic potentials with increasing Mg^{++} concentration. The detrimental effect of magnesium on charge capacity is also clear in the substantial decrease of anodic and cathodic

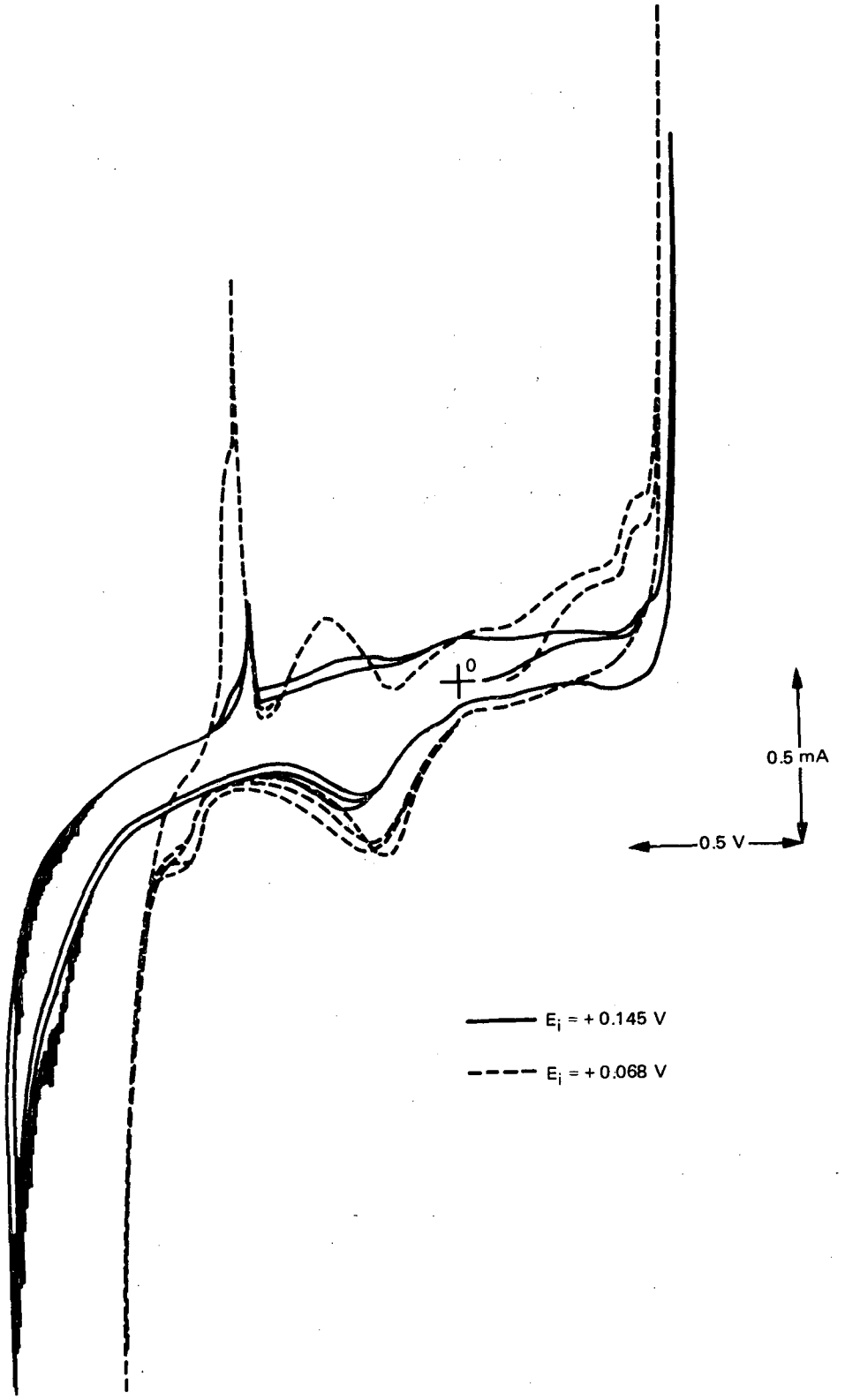
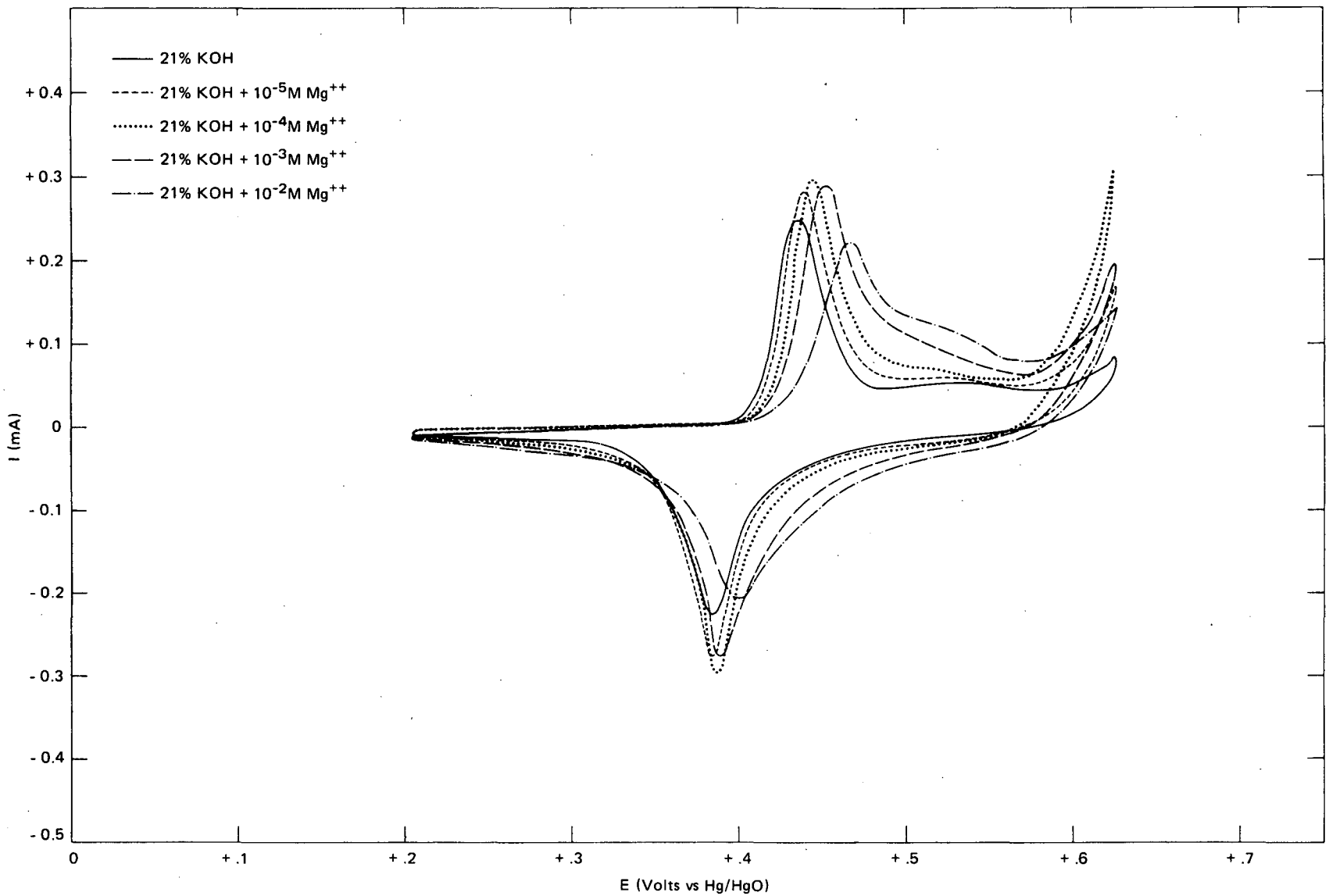
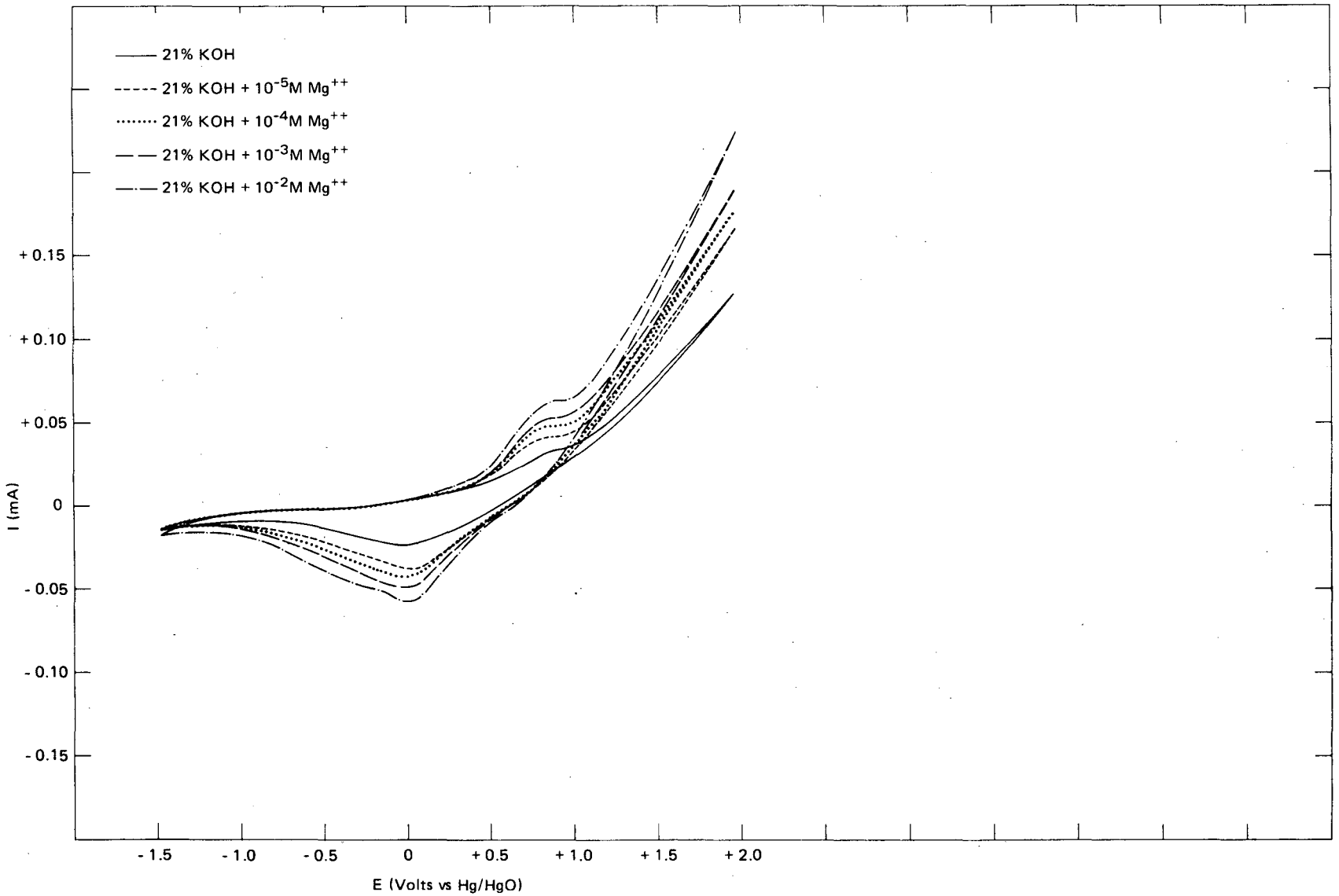


FIGURE 7 CYCLIC VOLTAMMOGRAMS ON A NICKEL ELECTRODE



(a) BARE Ni ELECTRODE

FIGURE 8 EFFECT OF LEAD ADDITIVES ON CYCLIC VOLTAMMOGRAMS, 50 mV s^{-1}, AREA = 0.15 cm^2



(b) NiO (SINGLE CRYSTAL)

FIGURE 8 EFFECT OF LEAD ADDITIVES ON CYCLIC VOLTAMMOGRAMS, 50 mV s^{-1}, AREA = 0.15 cm^2 (Concluded)

current peaks in Figure 8(a). Mg^{2+} is a small cation (0.65 Å), but it obviously is acting as an oxygen catalyst and a poison for the nickel reaction and in that manner reduces the NiO capacity.

Zinc

Compared to the number of studies on nickel, much less has been done to understand the effect of additives on zinc electrode behavior. Two major topics are of interest here: one is the reduction of the solubility of the zincate material and the other is to minimize the hydrogen overpotential.

We usually studied three types of nickel electrodes having different thicknesses of the active material ("bare nickel" electrodes, single crystal electrodes of NiO, and C-type films) in order to distinguish between the bulk and surface effects of various additives. In the case of the zinc electrode, we experimented only with "bare zinc" electrodes and single crystals of ZnO. Because of the fast dissolution of the zinc oxide and the very high cost of the ZnO single crystals, we had to limit our experiments with ZnO single crystals.

Last year we were able to construct an interfacial energy diagram for the interface Ni/NiO/alkaline electrolyte (2). Such a band diagram allows the researcher to predict the feasibility of important reactions such as hydrogen evolution, oxygen evolution, and anodic and cathodic decomposition, and sometimes to decide which reactions will dominate. On the basis of data from the literature on ZnO single crystals [band gap 3.2 eV and flatband potential +0.2 eV vs SHE at a pH of 4.8 (see ref. 15)] and a calculation of the ZnO cathodic decomposition potential by Gerisher (16), we have also constructed such a band diagram for ZnO. This diagram and the one for NiO are shown in Figure 9. The diagrams for the interfacial energies of NiO and ZnO are displaced with respect to each other by about 3 V. With NiO, the cathodic decomposition level falls within the band gap; if there are electrons in the conduction band, the material can be reduced. In the case of NiO, which is a p-type semiconductor, we have demonstrated that such a cathodic decomposition indeed takes place under illumination or with very negative bias, as expected for a highly doped p-type material. In the case of the ZnO, which is an n-type material (see below), the cathodic decomposition potential is above the conduction band edge, and therefore the reduction of ZnO is thermodynamically unfavorable. The reason why it occurs experimentally is explained by Morrison (15): When the ZnO becomes very negative, the Helmholtz potential is affected by the applied potential and the reduction becomes possible. [(In Figure 9 that translates into a shift of E_c(ZnO) with respect to $E_{c,d}$ (ZnO).] With the very conductive ZnO material used in battery plates, this explanation is very easy to accept, because the Helmholtz potential will be influenced by the applied potential even at relatively low cathodic potentials.

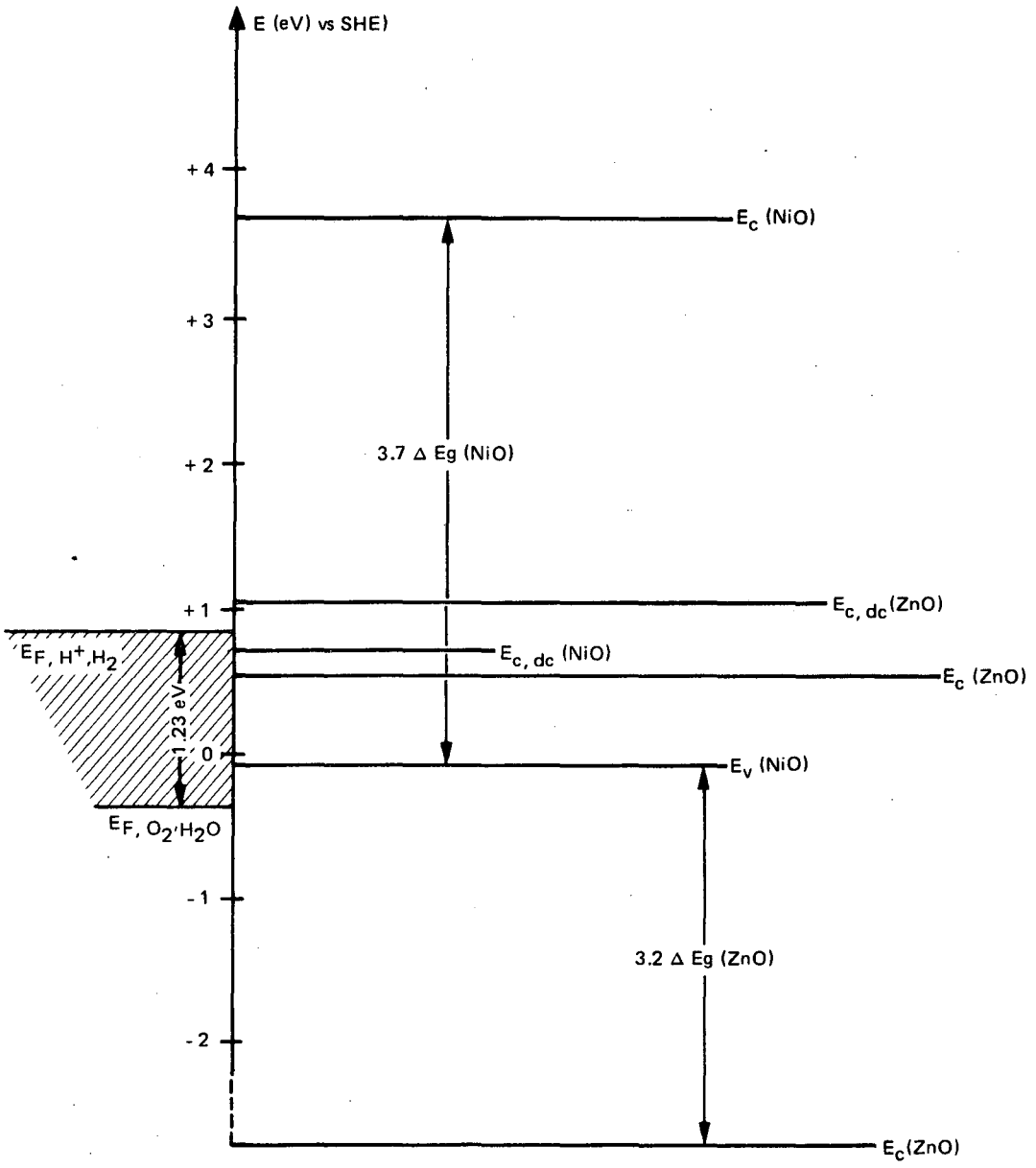


FIGURE 9 ENERGY DIAGRAM FOR Ni (II) OXIDE AND ZnO AT pH = 14 TOGETHER WITH FERMI-LEVELS FOR CATHODIC DECOMPOSITION ($E_{c,\,cdc}$), H^+/H_2 AND O_2/H_2O

Iron

Iron is a known deleterious impurity for NiO; it decreases the oxygen overpotential. We observed on the "bare zinc" electrode a large decrease of the hydrogen overpotential [Figure 10 (a)], which explains the negative effect of this same impurity on the zinc electrode. On the single crystal ZnO [Figure 10(b)], the oxidation/reduction is quite different and the effect of the iron impurity is small. The additional sharp anodic peak in this cyclic voltammogram (compared to the bare zinc) we associate with hydrogen oxidation, and we also assume that in this case the zincate reduction coincides with the hydrogen evolution reaction.

Fluoride

Solutions such as 15% KOH, 1% LiOH with saturated ZnO and 15% KOH, 1% KF, saturated LiOH have been used by LBL researchers to improve the zinc electrode performance. We have shown that both these solutions are quite detrimental to a nickel electrode that one would be using in the Ni/Zn cell. Here we describe their effect on the zinc electrode.

Figure 11(a) and (b) illustrates the effect of the fluoride addition on a "bare zinc" electrode. The relative magnitude of the currents in the case of the fluoride-containing electrolytes is much less (a factor of 10), and after an experiment in these fluoride-containing solutions a brownish film was observed on the electrode surface. Obviously the passivating film is more passivating in the presence of fluoride ions than when no fluoride ions are present. Our impedance measurements (see below) show that the films in the presence of fluoride are indeed more resistive. In general, our experiments indicate only negative effects from the addition of fluoride to the alkaline electrolyte. However, discharge of Ni/Zn cells is not limited kinetically by the zinc electrode, and additional polarization at the Zn/electrolyte interface can be tolerated if the suppression of zinc dissolution which causes it, results in an increased cycle life as has been proposed by LBL.

Zincate

Secondary silver-zinc and nickel-zinc cells are ordinarily filled with potassium hydroxide solutions saturated with zinc oxide. The addition of zinc oxide has the physical effect of somewhat reducing the conductance of the electrolyte, and the limiting current density decreases when the KOH electrolyte is saturated with zinc oxide (probably because the layer of zinc hydroxide formed on the electrode is less able to dissolve when the electrolyte is saturated with zincate.) Zincate is not really an additive but will necessarily be present when using a zinc electrode in an KOH electrolyte. In previous studies we have demonstrated that the discharge rate of zinc electrodes is increased in the presence of zincate, due to the autocatalytic nature of the discharge process (17-20).

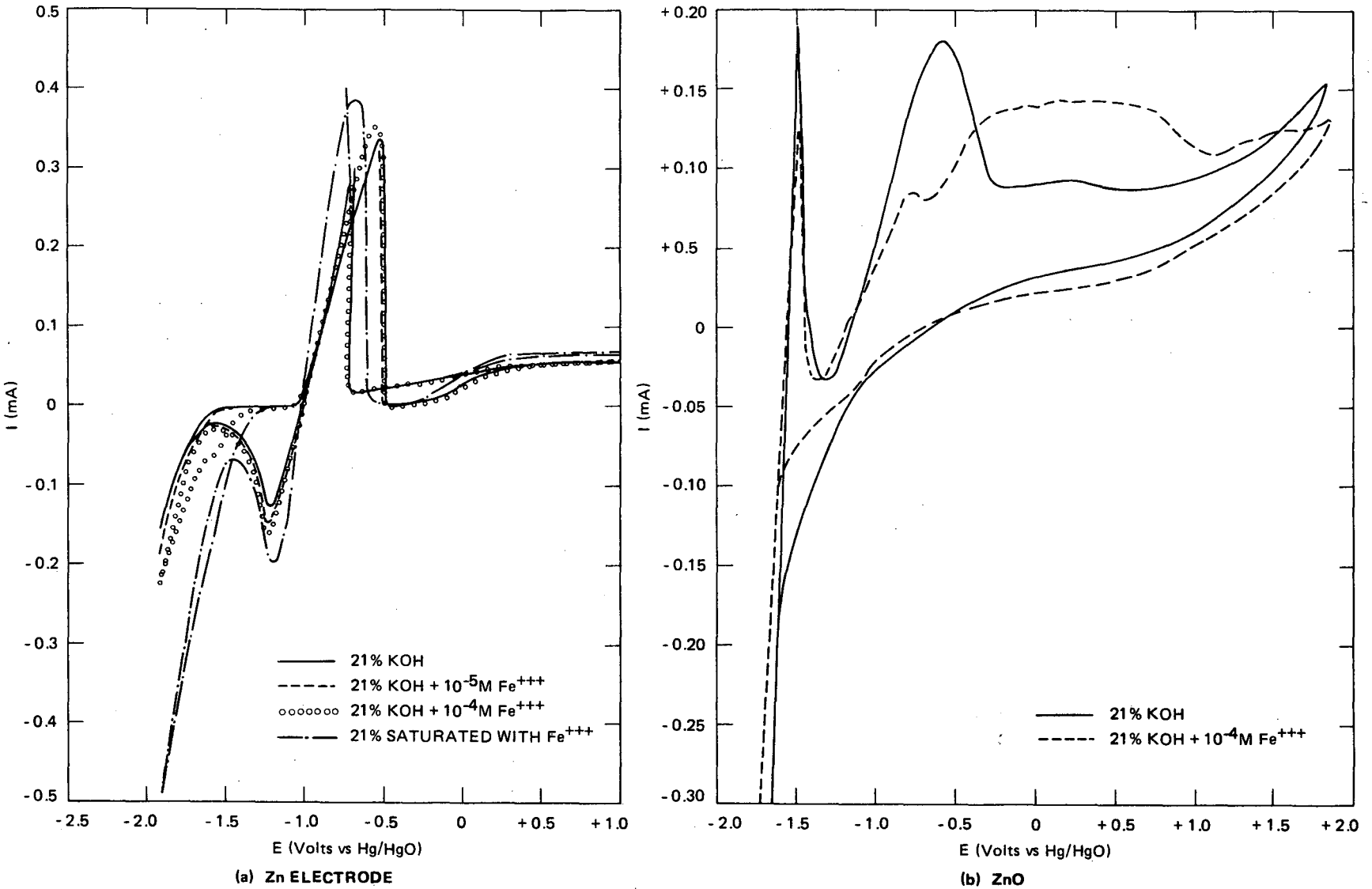
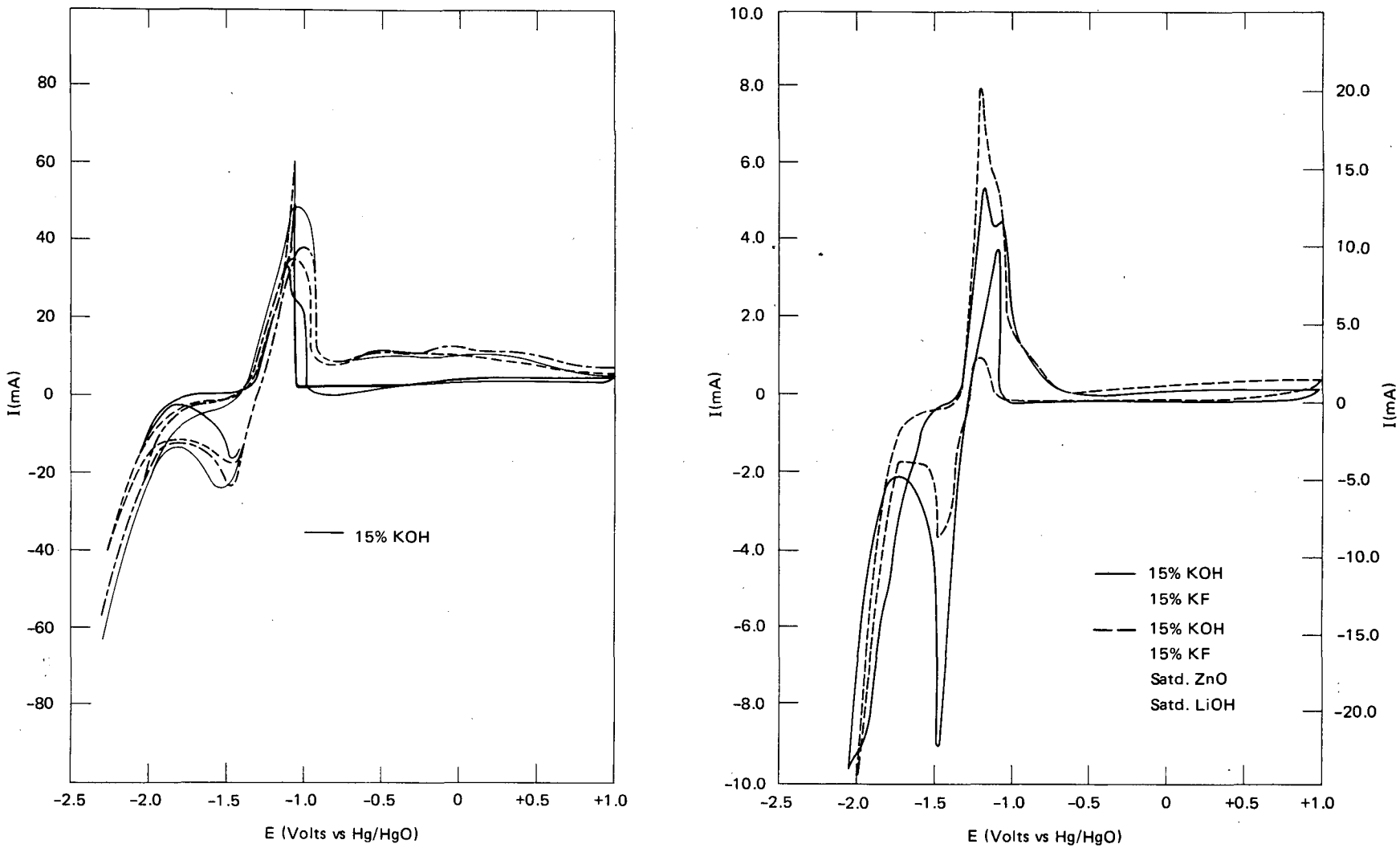


FIGURE 10 EFFECT OF IRON ADDITIVES ON CYCLIC VOLTAMMOGRAM, 50 mV s^{-1}



(a) Zn ELECTRODE

(b) Zn ELECTRODE IN FLUORIDE-CONTAINING ELECTROLYTES

FIGURE 11 EFFECT OF FLUORIDE ADDITIVE ON CYCLIC VOLTAMMOGRAMS, 50 mV s^{-1}, AREA = 0.1256 cm^2

Figure 12 demonstrates the zincate influence on cyclic voltammograms of zinc electrodes. The zincate concentration added to the alkaline solutions was varied from 0.001 to 1% by weight. We can see that at very low zincate concentrations (up to 0.01%), the hydrogen evolution is smaller than that obtained with a zincate-free solution, then the gas evolution increases with increasing zincate content, and the charging peak height is also substantially increased. The observation of a decreased hydrogen evolution at low zincate concentration was also reported for amalgamated zinc electrodes (21); the effect is not understood.

PbO

Figure 13 shows the effect of PbO on the performance of the zinc electrode. Dissolving 2% PbO in a 30% KOH solution leads to a distinct increase in the capacity of the zinc electrode, and increases the hydrogen overpotential. Both factors are beneficial for zinc as a battery electrode. We have seen before that PbO also has a beneficial effect on the nickel electrode, and dissolving some PbO in a Ni/Zn cell seems like a good strategy for improving the battery performance of that cell. Although we could show that in the case of the nickel electrode the PbO is electroactive in the range where NiO is being oxidized and reduced, this is probably not the case here (see Figure 7).

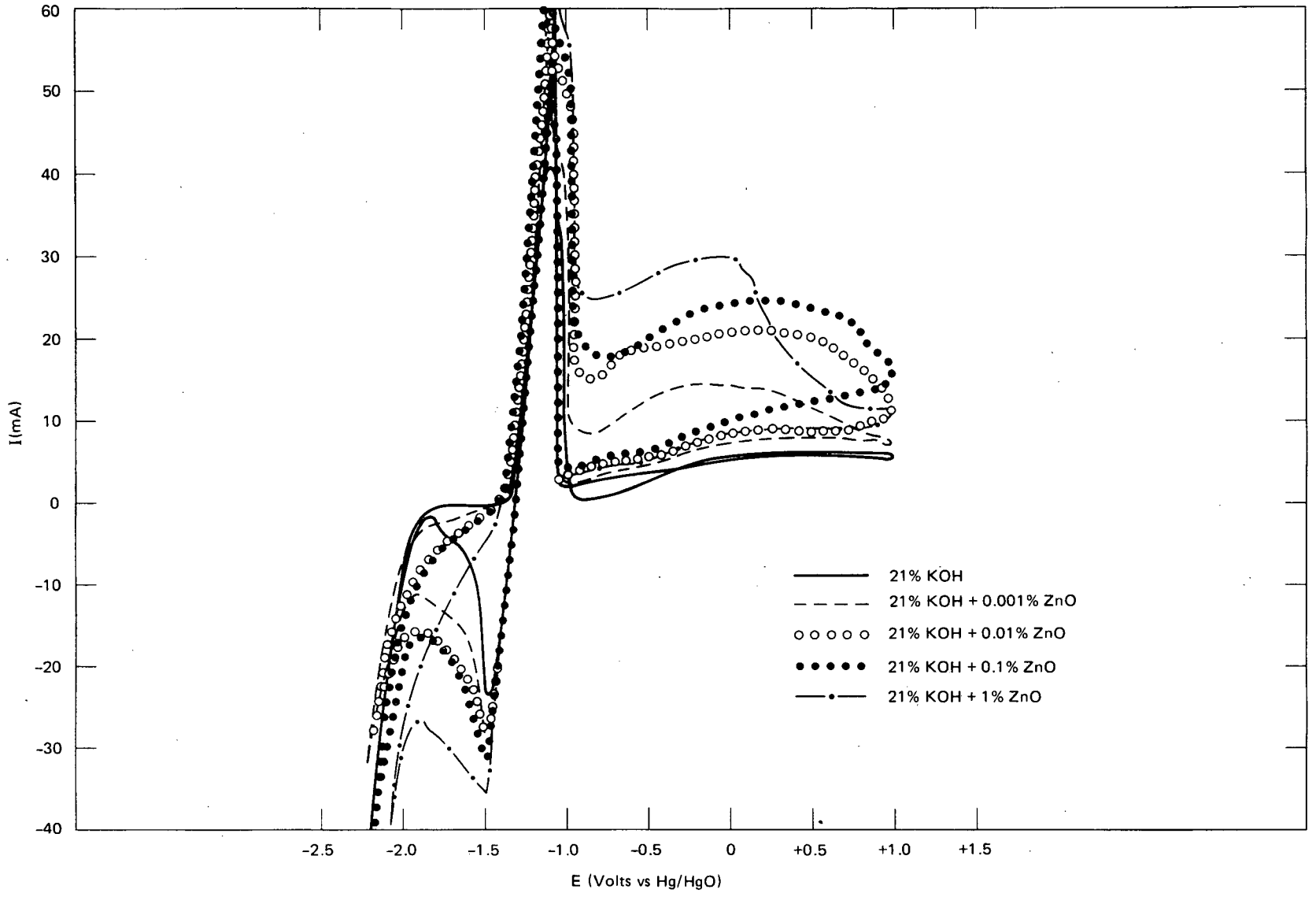


FIGURE 12 EFFECT OF ZINCATE ADDITIVE ON CYCLIC VOLTAMMOGRAMS, ZINC ELECTRODE, 50 mV s^{-1}, AREA = 0.1256 cm^2

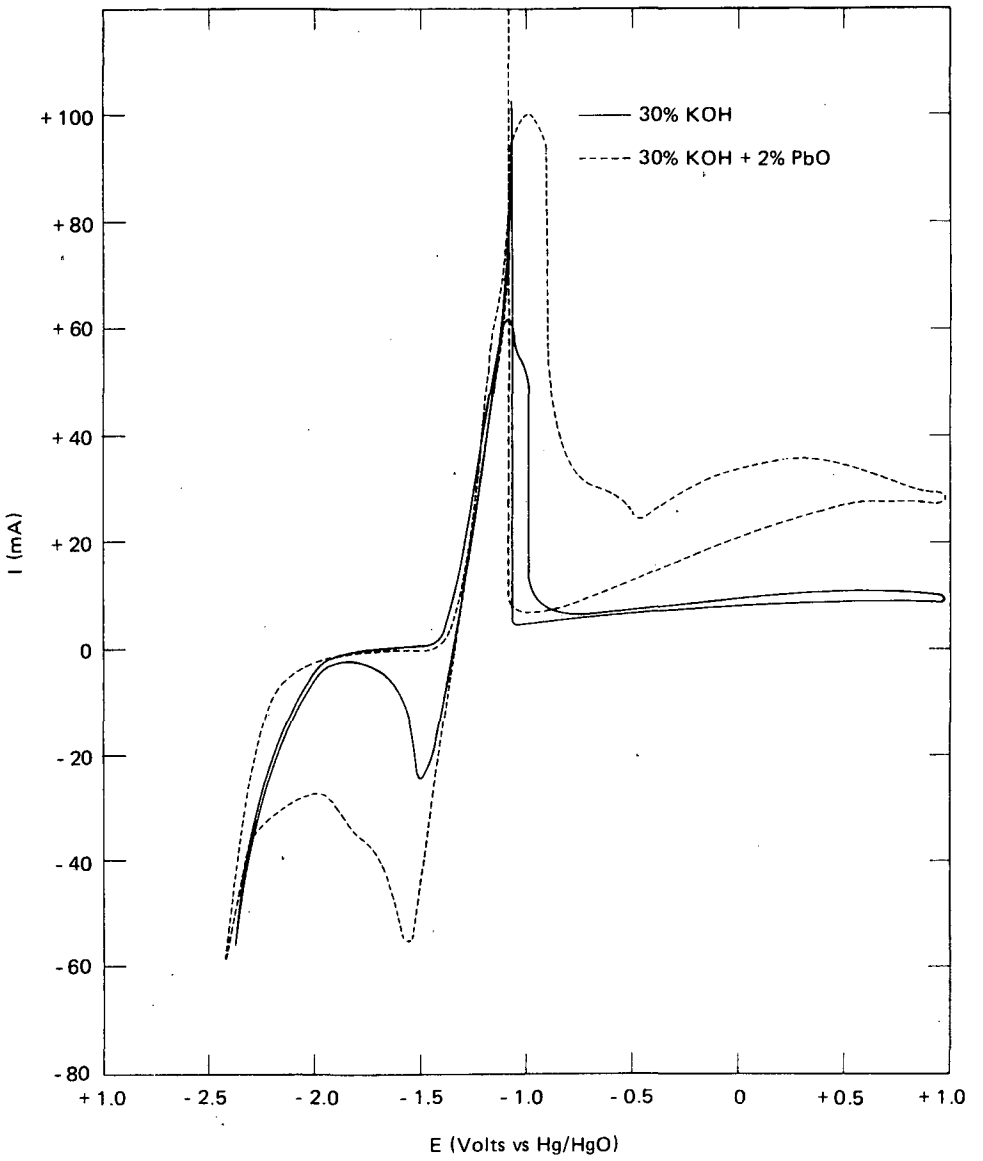


FIGURE 13 EFFECT OF LEAD ADDITIVE ON CYCLIC VOLTAMMOGRAMS, ZINC ELECTRODE, 50 mV s^{-1}, AREA = 0.1256 cm^2

IMPEDANCE MEASUREMENTS AND PHOTOEFFECTS

Nickel

Impedance measurements and photoeffects on nickel electrodes were reported last year (2).

Zinc

This year we have performed some preliminary impedance and photo experiments on zinc. As in the case of nickel, the impedance measurements and the photocurrent measurements are intended to provide detailed information about the nature of the interface electrode/electrolyte as well as about the kinetics of the important battery processes. We hope to be able to expand our efforts in this area next year.

Figure 14 shows a typical experiment on the photoeffects of zinc electrodes. The current through the cell is plotted as a function of time, while the light striking the electrode is being chopped with a mechanical chopper. The bottom curve in this figure is taken with the electrode at -0.8 V vs Hg/HgO (this is in the passive region), and it exhibits an anodic photoeffect increasing as a function of time without increasing the light intensity.

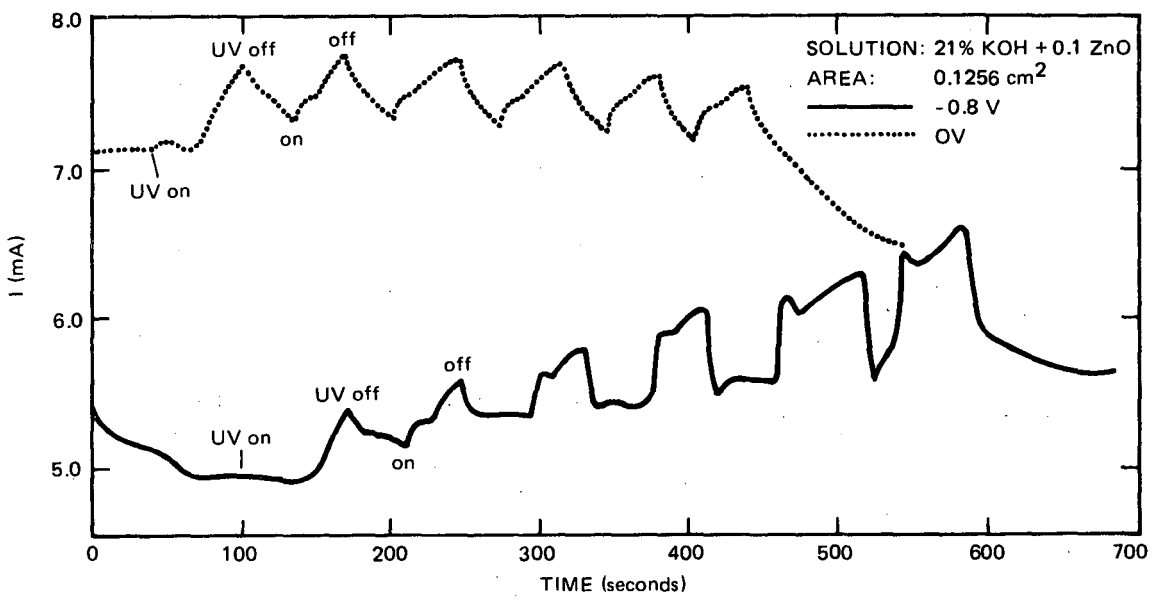


FIGURE 14 PHOTOEFFECTS OF LEAD ON ZINC ELECTRODE

This experiment indicates that the zinc oxide film here behaves as an n-type semiconductor, and it reveals that, as a function of time, this oxide film exhibits better and better photo properties. Improved photo properties implies a fundamental change of the zinc oxide passive material as a function of time at anodic potentials. It is not yet clear whether this effect is actually photoinduced or whether it is indeed a phenomenon that takes place whenever such a zinc oxide material is left at anodic potentials for some time. Also very intriguing is that the photocurrents exhibit two separate features, as if there were two separate photoprocesses involved (possibly associated with two phases of the zinc oxide material). There is indeed evidence that the passive layers on zinc have a duplex structure, with a thin, compact component beneath a porous one (21). At a potential further into the passive region, the same phenomena were observed. To identify the different oxide phases, experiments of the photocurrent as a function of the wavelength have to be performed. With this method we have a chance of revealing the electrical nature of the various oxides that are of interest on the passive zinc electrode, but obviously more experiments are needed.

Many impedance studies were carried out for zinc electrodes but most of them involved the active regime (17,23). Aurian-Blajeni and Tomkiewicz (22) recently attempted such a study. Our aim was also to characterize the passive zinc electrode by impedance measurements. Figure 15 shows a typical Nyquist plot for the passive zinc electrode in a 15% KOH, saturated LiOH, saturated ZnO solution (potential is -0.8 V vs Hg/HgO). Comparing this with the Nyquist plot of a passivated zinc electrode in a 15% KOH, 15% KF solution in Figure 16, it is obvious that the fluoride-containing film exhibits a higher impedance. The first semicircle in the Nyquist plot points toward a higher equivalent resistance (R_p) and a smaller equivalent capacitance (C_p), meaning that the fluoride electrolyte film is either thicker or has a smaller dielectric constant. However, both of the Nyquist plots look very similar to the ones obtained on a discharged nickel electrode; i.e. first we have a semicircle that is related to the passive film and electron transport through that film (at the high frequency range) and then we have a large onset of a diffusional process of ions through the passive film (at the low frequencies).

Making a more detailed study of these impedance characteristics in realistic battery solutions would be a useful tool to understand the nature of the passive zinc oxide films in these various solutions. We hope to be able to explore impedance and photocurrent measurements on the passive and active zinc electrode in more detail next year.

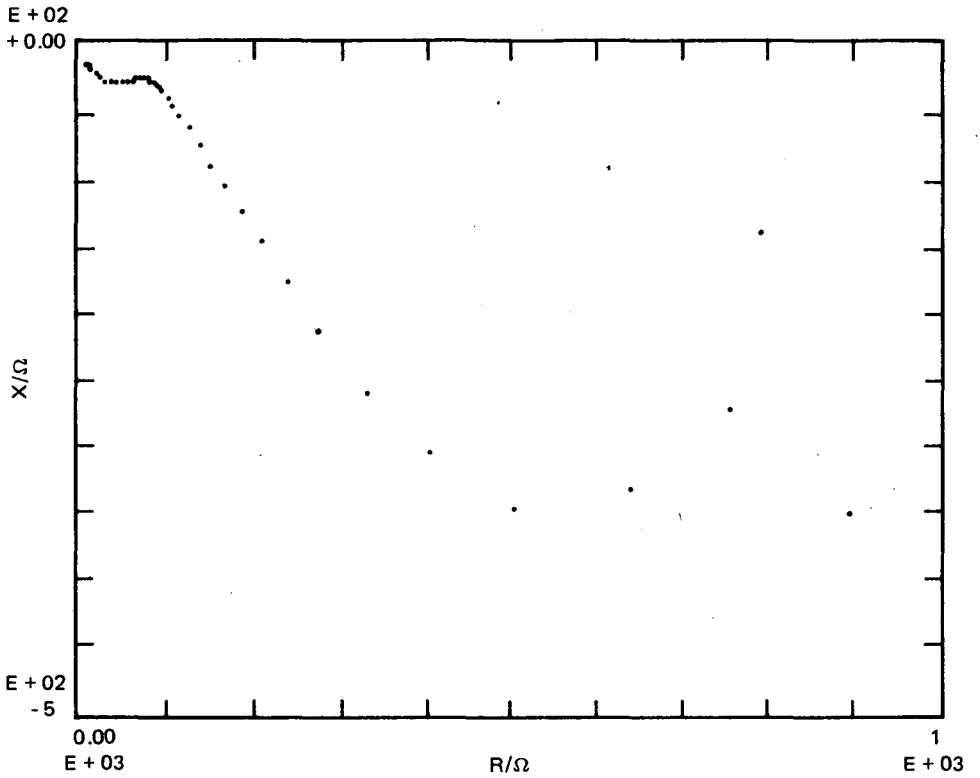


FIGURE 15 NYQUIST PLOT FOR APPLIED POTENTIAL OF - 0.8 V vs Hg/HgO
Solution: 15% KOH, saturated LiOH, saturated ZnO

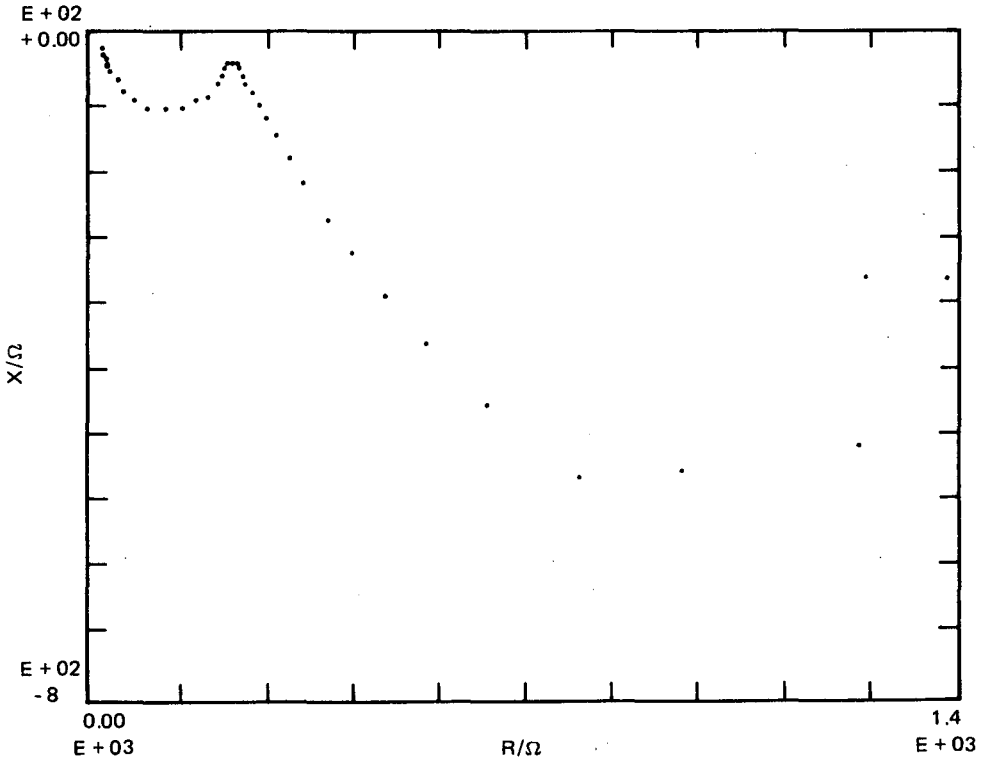


FIGURE 16 NYQUIST PLOT FOR APPLIED POTENTIAL OF - 0.8 V vs Hg/HgO
Solution: 15% KOH, 15% KF

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