

TECHNOLOGICAL IMPLICATIONS IN STUDIES OF NICKEL ELECTRODE PERFORMANCE AND DEGRADATION

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Summary

Several processes that are significant in sintered nickel electrode performance and degradation are addressed. The buildup of residual capacity is discussed in terms of the formation of a boundary layer between the current collector and the undischarged active material. The resistance characteristics that accompany the formation of the layer are presented, and the effects of changes in active material resistance and structure are correlated with electrode performance. Processes that can control nickel electrode recharge efficiency are also discussed, and data are presented indicating the kind of performance problems or changes that can be caused by changes in the interfacial morphology and physical structure of the active material deposit. Data are also presented indicating how variations in the composition of the active material can result during electrochemical deposition of active material into nickel electrodes.

Introduction

The nickel electrode is capable of operating with high efficiency for an extremely long cycle life as the positive electrode in nickel/cadmium, nickel/hydrogen, as well as other alkaline battery cells. However, some conditions encountered in the fabrication or management of nickel electrodes can cause significant degradation in performance. The purpose of this study is to better define some of the processes that contribute to loss of performance, and to determine the implications of these processes for improving nickel electrode performance.

Nickel electrodes are often observed to deliver a significant residual fraction of their capacity at voltage levels about 0.3 V below the primary discharge plateau. This phenomenon has been interpreted by Barnard *et al* [1] to result from the formation of an insulating barrier layer of divalent nickel hydroxide between the charged active material and the current collector. Recent measurements of nickel electrode kinetics [2] indicate that a depleted layer of active material does form at the current collector/active

material interface, and that this layer is responsible for residual capacity in the nickel electrode. The effects of an increase in residual capacity typically show up as a loss of usable capacity during discharge. Significant residual capacity has been observed in both Ni/Cd and Ni/H₂ cells [3 - 5] and it is expected that the residual capacity is due to the nickel electrode. This study reports data correlating both the resistance characteristics and the morphological characteristics of the active material in the nickel electrode with increases in residual capacity. Electrode discharge performance is shown to be largely controlled by the structure and composition of the interfacial region at the boundary between the current collector and the active material. Control over the active material structure in this interfacial region can significantly influence electrode performance.

The efficiency of the nickel electrode is also highly dependent on the charging voltage of the active material relative to the oxygen evolution voltage. Additives have been used to increase the difference between the active material charging voltage and the oxygen evolution voltage [6], thereby increasing efficiency. Recharge efficiency depends significantly on variables such as current density, active material morphology, and the use of additives. Data will be presented indicating the effects of these variables on recharge efficiency. Changes in the relative area of the interface between the active material and the electrolyte are shown to significantly change the recharge efficiency of the nickel electrode. Control over changes in the morphology of this interface appears to be critical in maintaining good, long term performance.

Significant variability is often observed in the performance of nickel electrodes. Much of the variability in performance can be attributed to variations in electrode structure — variations that can be caused either by the stresses and reactions of cycling, or by the details of the electrode fabrication. Particularly for electrochemical impregnation processes [7 - 9], for which the deposition of active material is under kinetic control, it is possible to get significant electrode variability from the fabrication process. We will present some studies related to the variability in the active material deposit in electrochemically impregnated nickel electrodes. The results of these studies indicate some of the problem areas that can be important in controlling the active material deposit during electrochemical impregnation of nickel electrodes.

Experimental

The nickel electrodes used in this study were made by electrochemical deposition [7] into sintered electrodes or onto flat nickel sheets. Sinter porosity was 82%, thickness 0.762 mm, and sinter loading was typically 1.60 g/cm³ void. The impregnation process was generally done in a refluxing solution that was 60% aqueous (2M in Ni(NO₃)₂ + Co(NO₃)₂) and 40% ethanol by volume. The solution reflux temperature was about 85 °C. Electrodes of

1 cm² area were typically made by deposition at 35 mA for 3 h. Charge and discharge rates are expressed as a fraction of C , which is the actual capacity of the electrode measured at a discharge rate of 15 mA/cm² to -0.5 V vs. Hg/HgO and was typically 25 - 30 mA h (90 - 108 coulombs) for recharge at a 15 mA/cm² rate

Electrodes were cycled in a closed, flooded laboratory cell that was continuously purged with nitrogen. The cell contained 32% KOH as electrolyte, and had an Hg/HgO reference electrode and a Ni sheet as a counter-electrode. All cycling and resistance measurements were done using a microprocessor-based controller for both control and data acquisition. The electrode resistance measurements were obtained from the electrode voltage response to a small amplitude step in current [10]. The amplitude of the current step was chosen by the computer to give about a 5 mV electrode response. The average oxidation state of the nickel electrode was estimated by assuming that discharge at the $C/200$ rate to -0.6 V vs. Hg/HgO left the active material essentially in a divalent state comprised of nickel hydroxide. Based on experiments involving further discharge at the $C/1000$ rate, such estimates of average valency are typically expected to be within 0.01 of the actual average oxidation state.

Relative nickel and cobalt concentrations in the electrodes were measured by atomic absorption spectrometry. Scanning Electron Microscopic (SEM) analysis was done on electrodes that were potted in epoxy, cross sectioned, and polished.

Nickel electrode residual capacity

The transient voltage response of the discharging nickel electrode to a small change in current may generally be resolved into two distinct time dependences. The first of these dependences is a relatively slow voltage relaxation that, at low current densities, is linear with $t^{1/2}$, and is consistent with a process exhibiting diffusion controlled kinetics [2, 10]. The resistance arising from this slow relaxation is attributed [2, 10, 11] to solid state conduction by proton diffusion in the active material lattice, and is referred to as the diffusion resistance of the nickel electrode in the following discussions. The second time dependence observed in the transient response of the nickel electrode is a relatively fast exponential dependence superimposed on the $t^{1/2}$ dependence. This dependence is consistent with a process exhibiting activation controlled kinetics, and has been attributed to the charge transfer process for nickel oxyhydroxide reduction above 0.2 V vs. Hg/HgO [11], and to boundary layer conduction below 0.1 V vs. Hg/HgO [2]. In the following discussions the resistance due to both of these activation controlled processes will be referred to as charge transfer resistance.

Nickel electrodes can build up significant amounts of residual capacity after extended use, as is indicated in Fig. 1 for a sintered nickel electrode that had undergone 1000 high rate (10 C) charge/discharge cycles. The shape of the discharge profile in Fig. 1 is largely controlled by the resistance

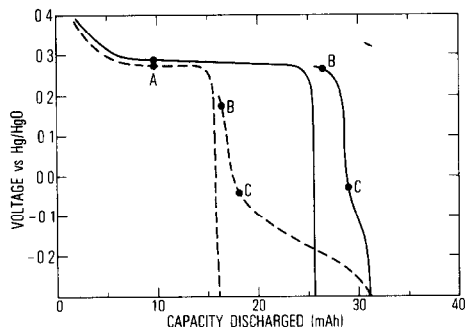


Fig 1 Nickel electrode discharge performance for a $C/2$ discharge followed by a $C/20$ discharge —, before cycling, ---, after 1000 high rate cycles Electrode was 1 cm^2 and contained a 5% cobalt additive

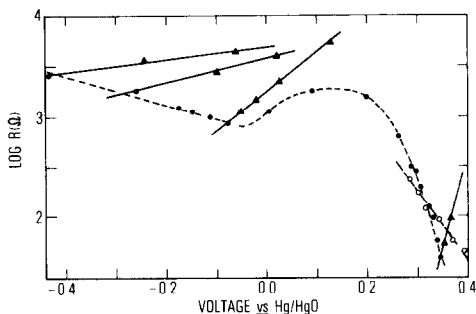


Fig 2 Resistance of a 1 cm^2 sintered nickel electrode as a function of voltage during a $C/100$ discharge of residual capacity (●) Diffusion resistance at higher voltages is represented by ○ At various times during discharge the charge transfer resistance was measured as a function of potential (—)

characteristics of the nickel electrode, rather than the changes in E_0 that can take place during reduction of the charged active material. The relationship of the various rate limiting processes [2] to the shape of the discharge voltage profile may be summarized as follows. During discharge at the $C/2$ rate on the upper voltage plateau (points A in Fig. 1), the diffusion resistance is dominant, indicating that proton diffusion within the active material controls the electrode polarization. During discharge of residual capacity at the $C/20$ rate at the upper voltage level (point B in Fig. 1) two processes control the electrode polarization. In addition to proton diffusion, the charge transfer resistance contributes significantly to the electrode polarization. The charge transfer resistance increases as the electrode is discharged, a trend that could be due to a decreasing charge transfer site density. When the charge transfer resistance reaches a critical level, a layer of poorly conductive material forms at the boundary between the current collector and the active material. When this layer forms, the voltage drops to the lower voltage plateau (point C in Fig. 1), and the resistive characteristics of the boundary layer control the electrode polarization. Continued discharge results in layer growth and a resultant decrease in voltage.

The changes in nickel electrode diffusion and charge transfer resistances that take place during discharge are indicated as a function of potential in Fig. 2. In the upper potential region where both diffusion and charge transfer resistances can be resolved, both are plotted as a function of potential. At the higher potentials, which correspond to average valence states of the nickel electrode above about 2.2, the diffusion resistance dominates the electrode resistance characteristics. The charge transfer resistance begins to dominate as the electrode discharges below about 0.3 V.

Plots of charge transfer resistance vs voltage at various fixed oxidation states are also presented in Fig. 2. The charge transfer resistance appears to

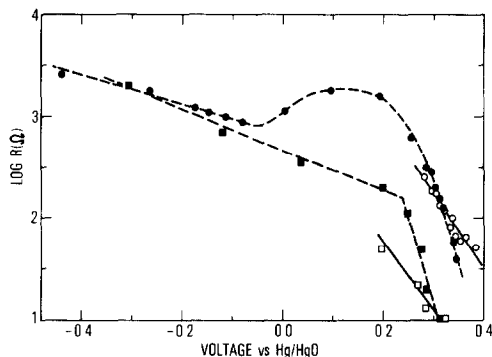


Fig 3 Resistance as a function of voltage for a nickel electrode (●) and a nickel electrode with 10% cobalt additive (■) during a $C/100$ discharge of residual capacity. The open symbols similarly indicate the diffusion resistances with and without cobalt at the higher voltages

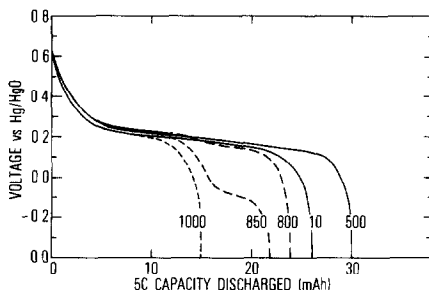


Fig 4 Discharge characteristics of a 1 cm^2 nickel electrode with no cobalt additive during 1000 cycles employing $5 C$ charge and discharge rates. The numbers on each curve indicate number of cycles completed

have a slope of about 60 mV/decade in the upper potential region, which is expected for a one electron charge transfer reaction. At about 0.2 V in Fig. 2, the electrode discharge drops down to the lower voltage plateau, and after a resistance peak during the drop in voltage, a new resistance function is established as the electrode discharges

Plots of resistance *vs* voltage are also presented in Fig. 2 at several points during the lower voltage discharge, and indicate a decreasing dependence of resistance on voltage as the residual capacity is discharged. It appears that as the active material approaches the divalent state it is also approaching a resistive condition for which the resistance is independent of voltage. The varying resistance/voltage slopes indicated in Fig. 2 result in a relatively complex current/voltage relationship for the lower voltage plateau at which the residual capacity is discharged. It is likely that the thickness of the boundary layer, as well as its resistance, is a function of current and cycling history. The net effect of these changes in current/voltage behavior is that the lower voltage plateau generally does not move to higher or lower voltages in a predictable fashion if discharge current is varied from cycle to cycle.

Additives can have a significant effect on the resistance of the active materials in the nickel electrode. The effect of a 10% cobalt hydroxide additive to the nickel electrode resistance is indicated in Fig. 3. The cobalt additive decreases the voltage of the electrode about 75 mV , thus shifting the resistance plots with cobalt to lower voltages in Fig. 3. The cobalt additive, however, has decreased both the proton diffusion resistance and the charge transfer resistance. The change in resistance makes the nickel electrode with cobalt as an additive much less susceptible to a buildup of residual capacity, by allowing a lower oxidation state to be reached before the

isolating layer forms at the boundary between the current collector and the active material. This is one reason why cobalt is an additive that is widely recognized as significantly improving the performance of the nickel electrode [12].

As was pointed out in the work of Barnard *et al* [1], the structure of the active material deposit and its area of contact with the current collector are extremely important in controlling the extent of residual capacity that can become isolated from the current collector. Decreases in the interfacial contact area are likely to result in the increase in residual capacity indicated in Fig. 1 that occurred as a result of extensive high rate cycling. In Fig. 4, the effects of high rate cycling on the discharge performance of a nickel electrode with no cobalt additive are indicated. After 500 - 600 cycles, during which the capacity gradually increased, the capacity suddenly began to fall and a second plateau began to form during the 5 C discharges. After 850 cycles, the lower discharge plateau was quite significant, and was decreasing in voltage with continued cycling. After 1000 cycles the material previously discharged during the lower plateau was no longer dischargeable at the 5 C rate, and only about one third of the lost capacity could be discharged at the C/20 rate. With cobalt present as an additive, as for the results in Fig. 1, this kind of degradation does not occur as rapidly or to as great an extent. It should be noted that the loss of capacity indicated in Fig. 4 did not correlate with shedding of active material from the electrode, and that it did not result from a decrease in the average valency of the charged electrode. Discharge at the C/250 rate to -0.6 V vs. Hg/HgO gave essentially all of the capacity present in the electrode before degradation was observed.

One explanation for the increase in residual capacity indicated in Fig. 4 is that the morphology of the active material at the current collector interface is changing as a result of the stresses of charge/discharge cycling. Both a decrease in the current collector/active material interfacial area and an increase in the average distance of active material from the current collector are physical changes that could contribute to the degradation indicated in Fig. 4. Strain measurements by Fritts [13] indicate that cobalt additives act to relieve the internal electrode stresses induced by charge/discharge cycling, and thereby may control the rate of capacity degradation from physical changes in the active material deposit.

The data presented and the mechanisms suggested here to account for excessive residual capacity in the nickel electrode also suggest ways to make electrodes less susceptible to this kind of capacity degradation. Cobalt, as an additive, has a major effect by decreasing the diffusion resistance of the active material. To realize the full benefits of such an additive, the additive should be put into the active material where it is most effective in delaying formation of a high impedance layer at the current collector interface. Such electrodes employ a cobalt gradient such that quite high cobalt concentration exists at the current collector, and the cobalt concentration decreases as the distance from the current collector surface increases. The performance

of this kind of "gradient electrode" has been previously described in detail [14], and has provided performance improvements early on in nickel electrode life of up to 10%. The general concept of additive control presents the possibility of controlling the physical location of additives in many other battery electrodes so that the additives will remain at the interface or location within the electrode where their presence is required to control degradation or to increase reaction rates.

Nickel electrode recharge efficiency

Many variables exist that influence the efficiency of nickel electrode recharge, but the primary requirement for efficient charging to occur is that a significant difference exists between the oxygen evolution voltage and the voltage at which the nickel electrode active material charges. The existence of multiple phases of charged and discharged active materials [15], each with its own voltage characteristics, therefore has a significant impact on charge efficiency [16]. It has also been shown that additives such as cobalt [17] can reduce the recharge voltage of the active material, and that materials such as lithium can improve efficiency by increasing the oxygen evolution voltage as well as reducing the active material charging voltage [18]. The recharge current can also significantly impact charge efficiency. It has been established that nickel electrodes can be charged to much higher oxidation states at higher current densities in laboratory cells [1, 19], as well as in sealed nickel/cadmium cells [20].

The higher recharge efficiency of the nickel electrode at higher current densities is of great practical interest, since if the higher efficiencies could be maintained at lower recharge currents the performance of the nickel electrode could be significantly improved. Several factors are important to allow high efficiencies for high rate recharge. First of all the structure of the active material lattice at the active material/electrolyte boundary is critical. This effect is indicated in Fig. 5 where the recharge characteristics of a nickel

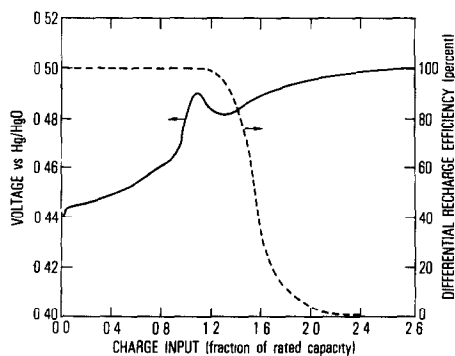


Fig 5 Voltage and efficiency during a $C/2$ recharge of a 1 cm^2 sintered nickel electrode with 10% cobalt additive. Efficiency was determined by discharge after various times to -0.5 V at the $C/5$ then $C/100$ rates

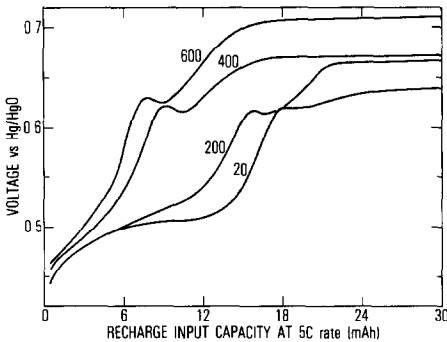
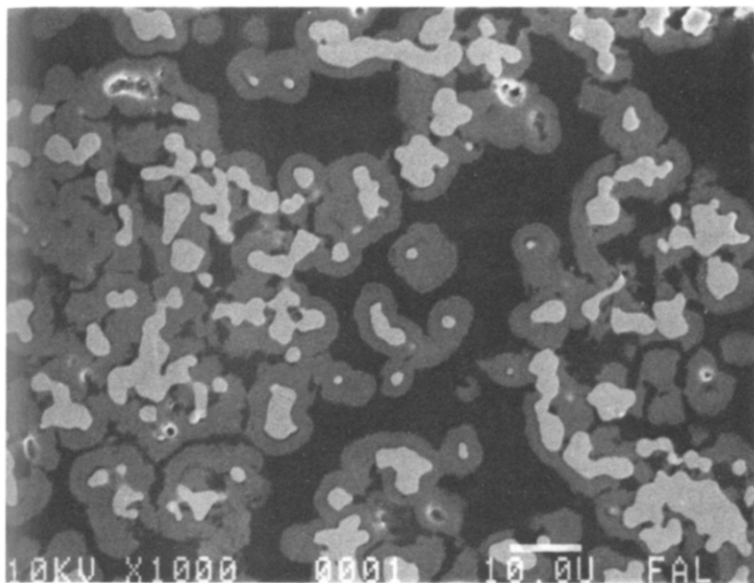


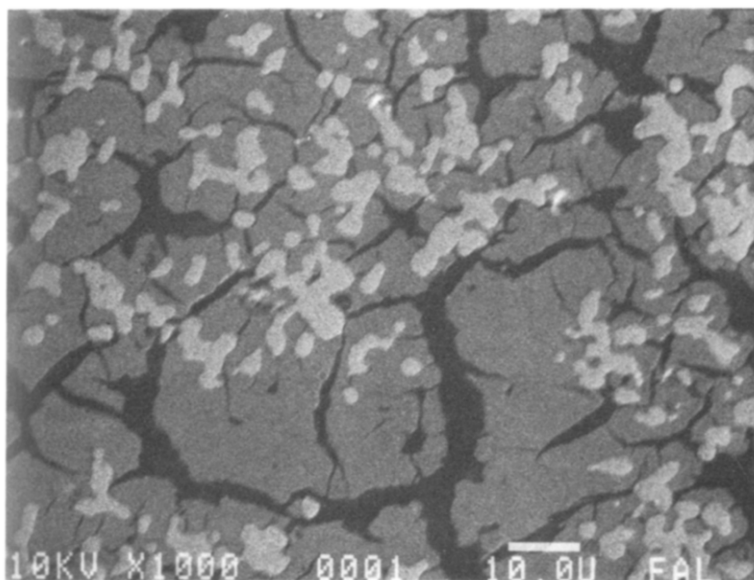
Fig. 6 Recharge voltage of a 1 cm^2 sintered nickel electrode during cycling using a $5 C$ charge and discharge rate. Cycle number is indicated on each curve.

electrode are indicated at a $C/2$ rate. What is most significant in Fig. 5 is that the ampere hour recharge efficiency remains essentially at 100% until well past the voltage peak or rollover, and only falls to zero as the recharge voltage approaches steady state oxygen evolution. The peak in the voltage profile is most likely due to the formation of a γ -nickel oxyhydroxide phase at the active material surface that becomes kinetically favored over oxygen evolution only at higher current densities. Complex behavior of Tafel slopes for oxygen evolution in the high potential region has been observed in the work of Conway and Bourgault [21], who have suggested both changes in surface coverage by active intermediates as well as actual changes in mechanism as possibly contributing to the observed behavior. The complex dependence of the Tafel slope for oxygen evolution on average oxidation state [21] may, in part, be due to the presence of both β and γ -oxyhydroxide phases, each having somewhat different voltages and oxygen evolution characteristics.

An additional factor that is important in recharge efficiency is the morphology of the active material. Oxygen is typically evolved at the surface of the active material at the electrolyte interface. The current density for oxygen evolution is therefore a function of the active material/electrolyte interfacial area, whereas the current density for active material recharge may depend on solid/solid interfaces within the active material. In Fig. 6 a nickel electrode recharge voltage profile is shown during high rate cycling that is expected to slowly change the morphology of the active material by the physical stresses of rapid charge and discharge. The voltage for steady state oxygen evolution increases steadily with cycling, while the recharge voltage prior to oxygen evolution does not change greatly. This effect can be attributed to agglomeration of active material such that the surface area for oxygen evolution is significantly reduced by the stresses of cycling. SEM micrographs of an electrode cross section after high rate cycling indicated that the active material was present as masses that largely filled the pores of the sinter, while prior to cycling a similar electrode had a less agglomerated active material morphology. Figure 7 shows the changes in



(a)



(b)

Fig. 7 SEM micrographs of cross-sectioned nickel electrodes ($\times 1000$). (a) Immediately after 5 formation cycles, (b) after 1000 10 C charge/discharge cycles. The white areas are Ni metal, gray areas active material, and the black areas are void regions.

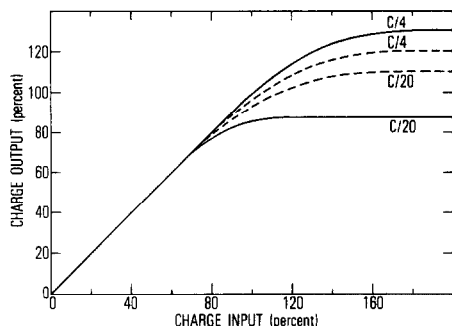


Fig 8 Nickel electrode capacity output as a function of capacity input for both $C/4$ and $C/20$ charge rates. Capacities are a percentage of initial theoretical capacity based on a one electron change — — —, prior to any high rate cycling, ———, the same electrode after 1000 5 C charge/discharge cycles. The electrode contained 10% cobalt additive. Capacity was measured by discharge to -0.5 V vs Hg/HgO first at $C/5$, then at $C/100$.

morphology that were observed in the micrographs. In addition, the capacity difference between a high charge rate and a low charge rate was also substantially increased by the stresses of high rate cycling, as indicated in Fig 8. The changes that are presented in Fig 8 are largely due to the changes in charge voltage relative to oxygen evolution at the high and low current extremes. In a system that tapers charge current at a given voltage level, the changes in Fig 8 would appear as a significant degradation of capacity.

The results in Figs. 5 - 8 suggest that significant variations in charge efficiency can occur as a result of variations in active material morphology that can change the contact area between the active material and the electrolyte. Significant differences are likely between the morphological changes induced by cycling and stresses in flooded laboratory cells, and the changes that occur in sealed, electrolyte-starved cells. However, the indication that morphology plays an important role in nickel electrode performance, and the fact that morphological or physical changes may often be invoked as reasons for battery electrode degradation, suggest that the control of active material morphology is critical both in battery management and in electrode fabrication.

Nickel electrode deposition

Electrochemical deposition of active material into nickel sinter can provide high quality electrodes with excellent life characteristics. However, these electrodes sometimes suffer from a high degree of variability in performance from batch to batch. Much of this variability can arise from the effects of morphological and physical variations in the active material deposit, such as those indicated in the preceding sections. The electrochem-

ical deposition process is essentially controlled by the deposition kinetics, with the rate of deposition depending on the relative rates of precipitation and dissolution within the sinter. The morphology depends critically on the net deposition rate and on the surface area on which the deposition is taking place, as well as many other variables such as temperature, concentration, and sinter surface oxides. Control over the active material structure obtained from electrochemical deposition, as well as an understanding of the processes that control the structure, are needed.

In studying techniques for control over the location of additives in nickel electrodes, it was found that the electrochemical deposition process can give rise to significant variations in additive concentration between the inner and outer regions of the active material deposit. This phenomenon was studied by electrodepositing active material onto flat plate nickel electrodes using a wide range of deposition conditions. The percentage of cobalt in the deposit, relative to that in the bulk solution, was measured. The results of this study are presented in Figs. 9 - 12, and display a significant variability in percentage cobalt as changes are made in rate, temperature, solution cobalt concentration, and ethanol concentration. While, in each Figure, significant variations in cobalt concentration occur as deposition conditions change, in all cases the weight of material deposited for a fixed coulombic input correlates directly with cobalt level. Clearly, at a higher rate of deposition either the precipitation of cobalt or the dissolution of nickel is favored. Figure 12 indicates that the cobalt level in the deposit approaches that in the bulk solution (10%) when no ethanol is added to the impregnating solution. This

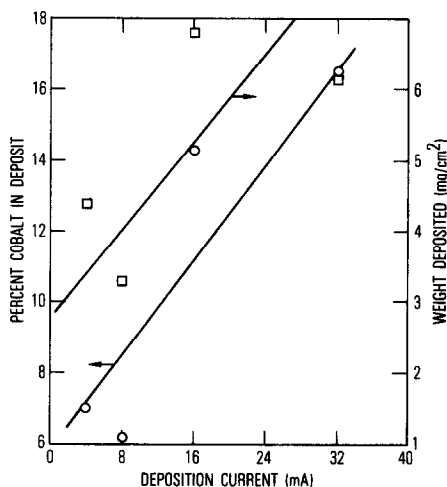


Fig 9 Cobalt content and weight of electrochemical deposit on a 1 cm² flat nickel plate as functions of deposition current. Solution was 60% aqueous (1.8M Ni²⁺, 0.2M Co²⁺) and 40% ethanol, 25 °C.

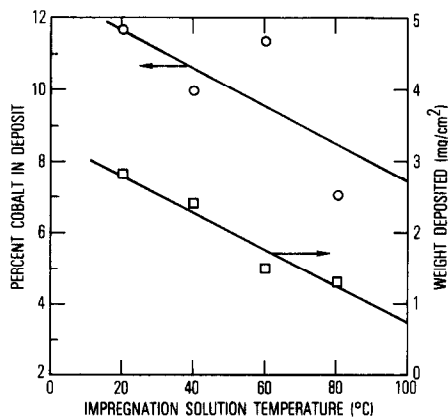


Fig. 10 Cobalt content and weight of electrochemical deposit on a 1 cm² flat nickel plate as functions of solution temperature. Solution was 60% aqueous (1.8M Ni²⁺, 0.2M Co²⁺) and 40% ethanol, deposition current was 8 mA for 30 min

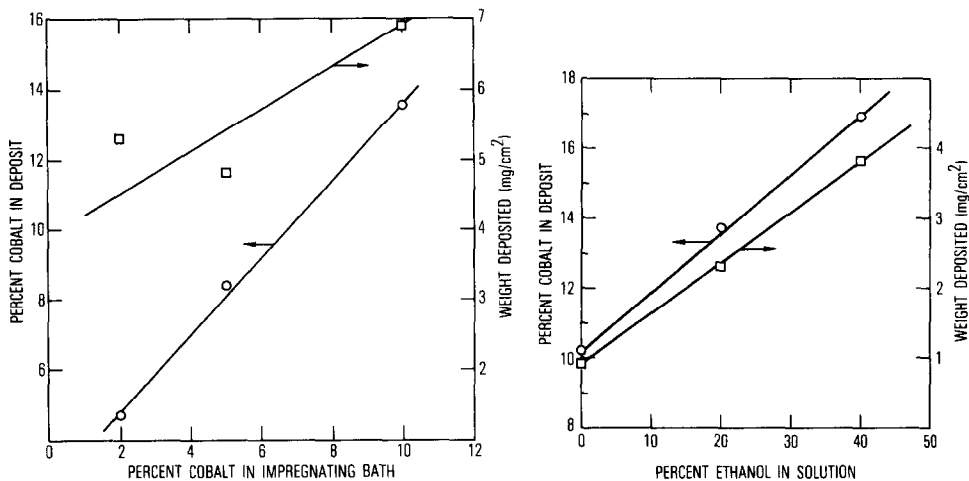


Fig 11 Cobalt content and weight of electrochemical deposit on a 1 cm² flat nickel plate as functions of cobalt content as a percentage of total Ni and Co in bulk solution. Solution was 60% aqueous (2M in Ni²⁺ and Co²⁺) and 40% ethanol, 25 °C, deposition current was 8 mA for 30 min

Fig. 12 Cobalt content and weight of electrochemical deposit on a 1 cm² flat nickel plate as functions of the solution ethanol concentration by volume. Aqueous fraction of solution was 1.8M Ni²⁺ and 0.2M Co²⁺, deposition current was 8 mA for 30 min, at 25 °C

suggests that ethanol is responsible for species that display different reactivities towards nickel and cobalt. Such species may be complexing agents produced during the deposition [7] such as amines or acetylacetone.

This study points out some of the possible problems associated with controlling the active material deposit during electrochemical deposition. Deposits may, in many instances, not be uniform throughout the sintered electrode. Data have been obtained suggesting that cobalt enhancement can occur on the outer surfaces of the sinter. Likewise, corrosion during deposition or electrode formation can result in a cobalt-depleted layer at the boundary between the sinter surface and the active material. Continued study in these and other areas will provide better definition to the processes that control electrochemical impregnation of nickel electrodes.

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