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NICKEL HYDROXIDE ACTIVE MATERIAL DENSITIES(U) AEROSPACE

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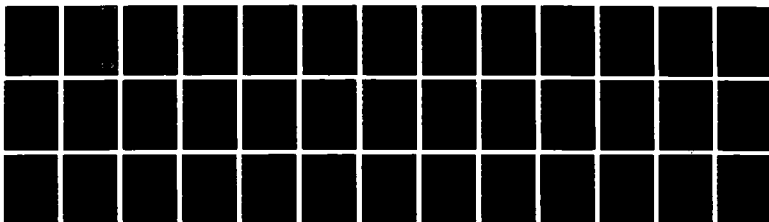
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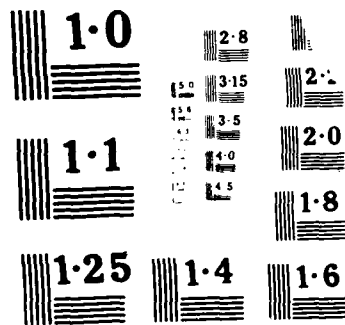
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Nickel Hydroxide Active Material Densities

A. H. ZIMMERMAN and P. K. EFFA
Chemistry and Physics Laboratory
The Aerospace Corporation
El Segundo, CA 90245

5 February 1988

Prepared for
SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Base
P.O. Box 92960, Worldway Postal Center
Los Angeles, CA 90009-2960

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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-85-C-0086 with the Space Division, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009-2960. It was reviewed and approved for The Aerospace Corporation by S. Feuerstein, Director, Chemistry and Physics Laboratory.

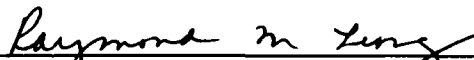
Lt Thomas Wetterstroem/CWA was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) Program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



THOMAS WETTERSTROEM, Lt, USAF
MOIE Project Officer
SD/CWASB



RAYMOND M. LEONG, Major, USAF
Deputy Director, AFSTC West Coast Office
AFSTC/WCO OL-AB

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) TR-0086A(2945-01)-3			5. MONITORING ORGANIZATION REPORT NUMBER(S) SD-TR-88-02		
6a. NAME OF PERFORMING ORGANIZATION The Aerospace Corporation Laboratory Operations		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Space Division		
6c. ADDRESS (City, State, and ZIP Code) El Segundo, CA 90245			7b. ADDRESS (City, State, and ZIP Code) Los Angeles Air Force Base Los Angeles, CA 90009-2960		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER FO4701-85-C-0086		
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
					WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Nickel Hydroxide Active Material Densities					
12. PERSONAL AUTHOR(S) Zimmerman, A. H. and Effa, P. K.					
13a. TYPE OF REPORT		13b. TIME COVERED FROM TO		14. DATE OF REPORT (Year, Month, Day) 1988 February 5	
				15. PAGE COUNT 41	
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	Energy storage systems /		
			Nickel sinter		
			Material compressibility		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
The density of nickel electrode active materials has been measured in situ as a function of the state of charge and operating conditions of the nickel electrode. Sintered electrodes made by both chemical and electrochemical impregnation methods were studied, and the effects of cobalt additives on the density and compressibility of the active material were determined. The results clearly indicate a phase transition that occurs when the active material is charged above an oxidation state of about 2.7. The transition involves large changes in the density, volume, and compressibility of the active material. Changes in density during open circuit stand, cycling, and trickle charging have been measured and the results correlated with the operating characteristics of nickel electrodes in battery cells.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

150-110

Accession For
NTIS GRA&I
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Unannounced
Justification by name and number

A-1

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I. INTRODUCTION

Nickel electrodes have been used in energy storage systems such as nickel cadmium, nickel zinc, nickel iron, and nickel hydrogen batteries for many years. In applications that require extremely long cycle life, the nickel electrode can become a life-limiting element. This is particularly true for long term aerospace applications in which the nickel cadmium and nickel hydrogen batteries are used. The nickel electrodes in these batteries consist of a sintered nickel substrate that is impregnated with a nickel hydroxide active material. As the electrode is charged and discharged, the active material can undergo significant expansion and contraction,¹ which can exert mechanical stress on the sinter structure and eventually cause physical damage to the electrode. The result of such mechanical stress is typically observed as swelling in the overall thickness of the electrode, a convenient measurement that is often used to indicate the susceptibility of sintered electrodes to internal stresses.

Changes in the volume or density of active material under normal conditions of nickel electrode operation can also create problems that are not associated with physical damage to the sinter structure. Typically as nickel electrodes degrade, they exhibit a fading capacity under conditions of high rate discharge.² The capacity fading may be caused by physical movement and agglomeration of the active material deposit in the pores of the nickel sinter. The physical separation of the active material from the surfaces of the pores diminishes its utility for high-rate electrochemical discharge. The changes in active material volume or density are generally recognized as contributing to these changes in performance characteristics; however, the changes in density or volume of nickel hydroxide active materials have not been studied in detail over the range of conditions over which nickel electrodes are used. Furthermore, no consistent picture has emerged as to the mechanisms by which changes in the lattice characteristics of solid-state active materials can create macroscopic physical movement of material in porous electrodes.

In this study, the volume and density of such active materials have been precisely measured over a wide range of states of charge and operating conditions. An in-situ measurement technique was employed so that the density and volume of the active materials could be measured in the actual operating nickel electrode environment. Active material characteristics were measured as functions of electrode oxidation state, presence of cobalt additive, charge and discharge profiles, and open circuit stand. The measured physical properties of the solid-state materials that comprise the nickel electrode can provide data that allow changes in nickel electrode performance to be understood in detail, and thus provide the important inputs required for a theoretical model of nickel electrode performance characteristics.

II. EXPERIMENTAL

The volume of the active material was measured by a gravimetric technique that involved measuring the difference between the weight of a dry electrode and the weight of that same electrode immersed in electrolyte of known density. The density was then obtained using the weight of the active material in the dry state. For these measurements to reflect the characteristics of the active material alone, corrections must be made for the nickel metal in the electrode, and for the weight of the nylon thread used to support the electrode in the electrolyte during weighing. The active material density is obtained from Eq. (1)

$$D_a = D_e (W_d - W_N) / (WD - V_N D_e) \quad (1)$$

in which D_a is the density of the active material in the sintered electrode, D_e is the density of the electrolyte, W_d is the dry weight of the electrode, W_N is the weight of the nickel metal in the electrode, WD is the weight difference between the dry electrode and the electrode immersed in electrolyte, and V_N is the volume of the nickel metal in the electrode. The value used in Eq. (1) for WD must be corrected for the weight of the thin nylon thread that was used to support the electrode in the electrolyte during the weighing process.

$$WD = W_d - W_w + W_{th} - V_{tw} D_e \quad (2)$$

In Eq. (2) W_w is the immersed weight of the electrode plus that of the supporting thread, W_{th} is the weight of the thread, and V_{tw} is the volume of the thread that is immersed in the electrolyte. An extremely light and thin nylon thread was selected to support the electrode so that the correction terms in Eq. (2) were always small. However, for high precision density measurements, these corrections could not be neglected. The weight of the air displaced when the electrode was immersed was not considered in these measurements, since it introduces only a small and nearly constant correction to the density in the third decimal place.

The active material density was most easily measured when a sufficiently large volume of active material was localized in a relatively small overall volume. The use of a single flat plate electrode required inconveniently large plate dimensions to provide an active material volume of at least 2 cm^3 , which was the volume required to obtain high precision measurements. Because the electrode must be physically similar to the electrodes used in battery cells so that similar charge and discharge conditions would apply, a special dual-plate electrode design was employed. This electrode consisted of two equally sized pieces of nickel sinter placed parallel to each other and welded together with nickel wires, with about 1.0 inches separating the plates. Total active superficial area was 80 cm^2 , with each plate being 4 by 10 cm.

The porosity of the sinter was 82%. The sintered plates had a typical thickness of 30 mils. Prior to impregnation of the electrode assembly, it was soaked in an EDTA solution to remove nickel oxides that might be present in the sinter, then weighed to determine the total amount of nickel metal present in the electrode assembly. Impregnation was done using either an electrochemical or a chemical technique. Electrochemical impregnation was done by cathodizing the assembly in a bath consisting of 60% 2 molar metal nitrate solution and 40% ethanol. The temperature during impregnation was the reflux temperature of the solution, typically about 80 degrees C. The cathodization current was 20 ma/cm^2 . After electrochemical impregnation, the electrode was rinsed, dried, and weighed to determine active material weight pickup. Chemical impregnation was done by repetitively dipping the electrode in a 2 molar metal nitrate solution followed by a dip in 20% potassium hydroxide. About 10-12 sequential dips were required to get the desired loading levels. The electrode was rinsed with DI water, dried, and weighed after every other dip to determine the accumulated loading.

Charging and discharging of the electrodes was done in 31% potassium hydroxide electrolyte at ambient temperature, 23 ± 2 degrees C. The electrodes were operated in the flooded state in a polystyrene container that was continuously purged with a slow flow of nitrogen to prevent contact with atmospheric gases. The counter electrode was a sheet of nickel metal. All electrode voltages were measured relative to an Hg/HgO reference electrode.

The reference electrode was enclosed in a polyethylene tube that dipped into the cell electrolyte at one corner of the test electrode. Electrolyte contact to the reference electrode was made through a fine nylon wick inserted through a small hole in the polyethylene tube that contained the Hg/HgO reference electrode. Test electrode cycling was typically done at constant current, using a computer to control and time the cycling as well as to monitor and plot the electrode voltages.

The computer was also programmed to measure the absolute state of charge of the electrode relative to the divalent, or totally discharged, state of the active material. Because it is very time consuming to discharge essentially all residual capacity from a nickel electrode, the totally discharged state was determined by an asymptotic technique. The electrode was discharged to -0.5 volts relative to the Hg/HgO reference at a rate of 1 ma/cm². Thereafter, the current was continuously reduced so that the voltage was held at -0.5, while the computer integrated the total amount of charge removed from the electrode. This discharge procedure for residual capacity was typically continued for 12 hours. The capacity that would have to be discharged to reach the divalent state of the active material was obtained by extrapolating the cumulative capacity discharged to zero discharge rate. This extrapolation was done by plotting the capacity discharged as a function of the square root of the discharge rate, since this plot was found to provide a function that could be conveniently extrapolated to zero discharge rate. Control experiments verified that this technique accurately indicated the approach of the active material to the divalent (or totally discharged) state. State of charge as used here is defined as the oxidation state of the nickel or cobalt in the active material that is in excess of 2.0 (divalent state).

Density measurements were done by first cycling the electrode to stabilize and determine its electrical performance under the selected conditions of operation. The first cycle involved charging for 10 hours at a C/10 rate (2 ma/cm²), followed by discharge at C/2 to zero volts (vs. Hg/HgO) and discharge of residual capacity, as described above, at -0.5 volts for a period of 12 hours. This procedure typically brought the electrode down to a state of charge of less than 0.05, where 0.0 corresponds to the totally

discharged state (assumed to be divalent nickel hydroxide) and 1.0 corresponds to a trivalent state. Oxidation states were calculated using the dry weight of active material to determine the number of moles of material present. The electrode was brought to the desired state of charge by either charging for a fixed period, trickle charging, or cycling. The capacity was then discharged to determine the actual state of charge reached. The electrode was then brought to the desired state of charge a second time for the active material density measurements.

The active material density was determined as a function of stand time for all electrodes, typically for up to 100 hours, although for several cases the density was monitored for up to 20 days. Each density measurement involved exposing the immersed electrode to a vacuum to draw all oxygen gas out of the pores; suspending the electrode by a nylon thread from an analytical balance while immersed; and weighing the electrode as a function of time for a period of 0.5 hour from termination of the vacuum exposure. In this way, the buoyancy effects of any internally generated and trapped oxygen at high states of charge³ could be easily removed by extrapolation of the weight to the time at which vacuum exposure was terminated. The electrode was weighed in the same electrolyte that it was allowed to stand in, and during the stand period, contact of the electrolyte with atmospheric gas was limited by bubbling nitrogen through the electrolyte. The electrolyte density was determined after each active material measurement by determining the weight of a 50 cm³ volumetric flask filled with the electrolyte. This technique was calibrated with bare nickel sinter, which gave the correct density to ± 0.004 g/cm³. The dry weight used for the active material was measured after rinsing the electrode in flowing DI water for 6 hours, followed by drying in vacuum at 40 degrees C for 16 hours.

The compressibility of the active material could be determined in situations where highly compressible active material structures were generated. The compressibility was measured by following the increase in density that resulted from removing the active material from vacuum to a 1 atm, or ambient, pressure. The high compressibilities that were measured in this way under some conditions may arise from the presence of small voids and

grain boundaries between the crystallites of active material, many of which may contain oxygen given off at high states of charge from both overcharge and self-discharge. This kind of structure involves macroscopic disorder similar to that in a fine powder, and is likely to be created by forces on the active material deposits that can fracture the otherwise relatively ordered masses of crystallites.

The density of active material was measured as described above with high precision, typically $\pm 0.005 \text{ g/cm}^3$. The accuracy of these measurements is contingent on several assumptions. First, it was assumed that all gas is removed from the pores of the electrode by the evacuation process. This assumption was checked by verifying some test cases for which the results did not depend on the time of exposure to vacuum. However, when very small spaces between active material crystallites are present, it is possible that gas filled space can remain through evacuation. Such effects will tend to give a very low density that will be similar to a powder density, as well as giving a significant compressibility. Another assumption was that the weight of the active material is not affected by the rinsing done prior to drying, except for removing potassium hydroxide that is not tied up in the solid lattice. Weakly bound water is not included in the weight since this is removed by the drying procedure.

III. RESULTS

A. INITIAL ACTIVE MATERIAL DENSITIES

The densities of the active material in nickel electrodes were found to vary significantly, depending on the technique used for electrode preparation and the presence of cobalt additive. Three different kinds of electrodes were prepared for this study. Chemical deposition and electrochemical deposition were used to deposit pure nickel hydroxide, and chemical deposition was used with 10% of the nickel replaced with cobalt. The loading levels were 1.32 g/cm³ void for the chemically deposited electrode containing pure nickel hydroxide, 1.42 g/cm³ void for the chemically deposited electrode containing 10% cobalt, and 1.69 g/cm³ void for the electrochemically deposited electrode containing pure nickel hydroxide.

The chemically deposited materials, as initially impregnated into the sinter, had a quite low density prior to any electrochemical charge or discharge. The density of the nickel hydroxide was about 2.60 g/cm³, and for the nickel hydroxide with 10% cobalt, about 2.02 g/cm³. The initial densities of the materials impregnated by chemical precipitation are likely to be dependent on the conditions of Ph, temperature, and ion concentration in the precipitating solutions. After the first charge/discharge cycle, the density of the pure nickel hydroxide in the discharged state increased to about 3.5. About 5-10 cycles of charge followed by total discharge were required to stabilize the density of the fully discharged nickel hydroxide with 10% cobalt at about 3.4 g/cm³. Somewhat different behavior was observed for the electrochemically deposited pure nickel hydroxide, which was initially deposited in a state having a density of 3.37 g/cm³. After a charge/discharge cycle, the density of this material in the fully discharged state was typically about 3.5. The low initial density of the chemically deposited material places limitations on the amount of material that can be impregnated into sinter, limitations that are not present for electrochemically deposited material. A practical consideration that can arise from this difference is that overloading of sinter with active material can occur more easily in the electrochemical process if not closely controlled.

The differences in the density of the active materials deposited chemically from that deposited electrochemically may be due to differences in the phase structure of the initially deposited material, or differences arising from crystallite or grain size. In work done by Barnard,⁴ it was concluded that an inactive form of α -Ni(OH)₂ resulted from chemical deposition while β -Ni(OH)₂ resulted from electrochemical impregnation. Measurements by Bode et al.⁵ have indicated that large density differences exist between α - and β -forms of Ni(OH)₂, both of which can exist in either active or inactive forms⁴ that differ primarily in their degree of lattice disorder. The presence of cobalt in the active material lattice may decrease density by either promoting the formation of α -Ni(OH)₂, or by introducing lattice defects in the form of cobalt ions. The large changes in density that occur upon initial cycling of chemically deposited materials are likely to involve significant reordering and stress within the solid deposit, and may be one reason for improved performance stability and active material utilization during cycle life that has been obtained for electrochemically impregnated nickel electrodes⁶. The higher initial densities of electrochemically deposited active material made deposition of the target loading of 1.6 g/cm³ void much more easily accomplished, and actually made it necessary to carefully control the deposition conditions to avoid overloading of the sinter.

B. OPEN CIRCUIT STAND EFFECTS

After all electrode operations that involved a net change in state of charge, the density of the active material was observed to relax from an initial value towards a significantly higher density during open circuit stand in the electrolyte. Typical changes in density during stand are indicated in Figs. 1 and 2 for the electrodes containing no cobalt additive. The greater range of density change indicated for the chemically impregnated electrode in Fig. 2 is likely to be caused by the higher utilization of active material in this electrode which results from the lower loading level. The higher utilization allowed significantly higher states of charge having more extreme

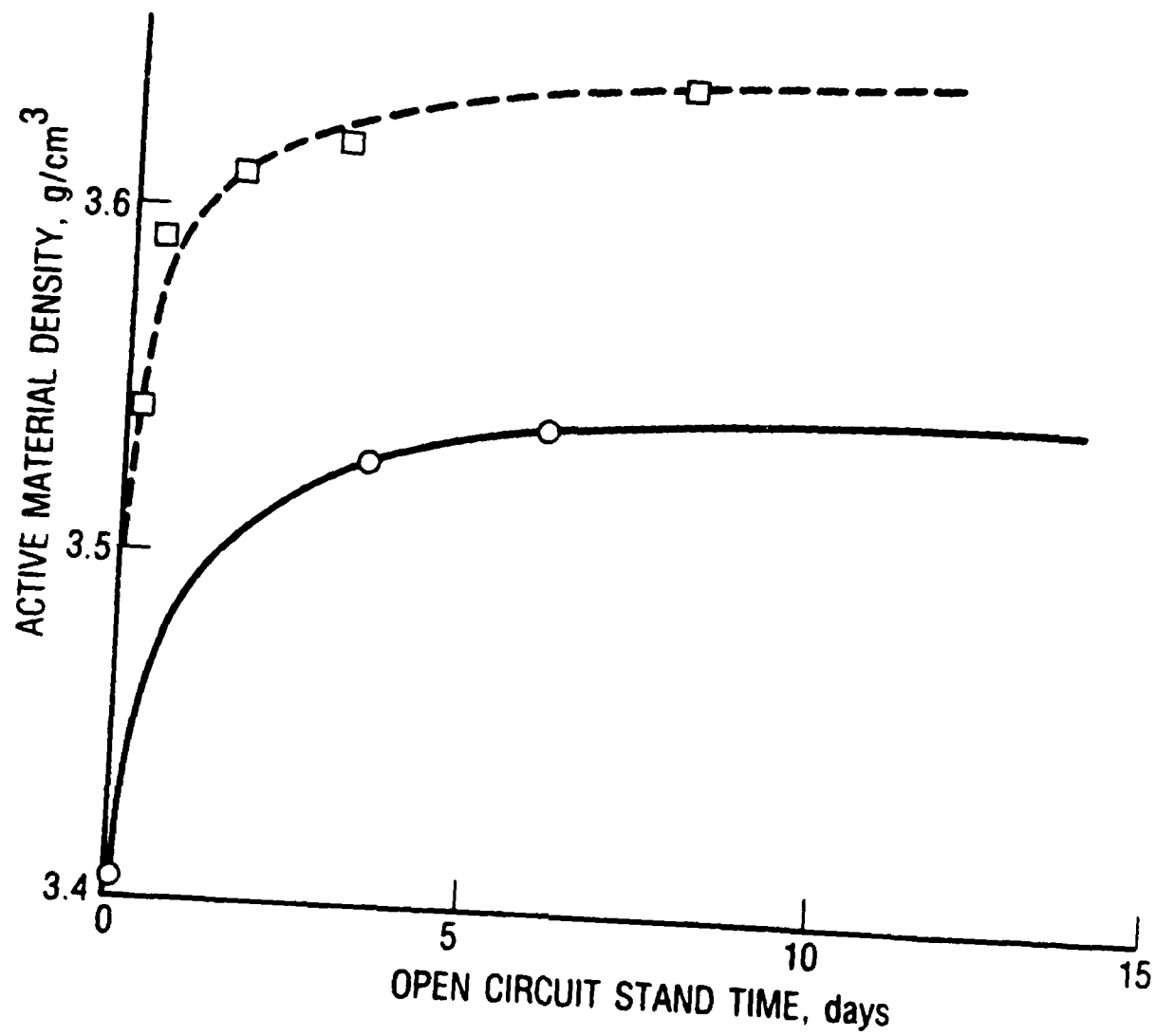


Fig. 1. Change in Density as a Function of Time During Open Circuit Stand in 31% KOH for an Electrochemistry Impregnated Nickel Hydroxide Electrode. The solid line is for a state of charge of 0.045 and the dashed line is for a state of charge of 1.021.

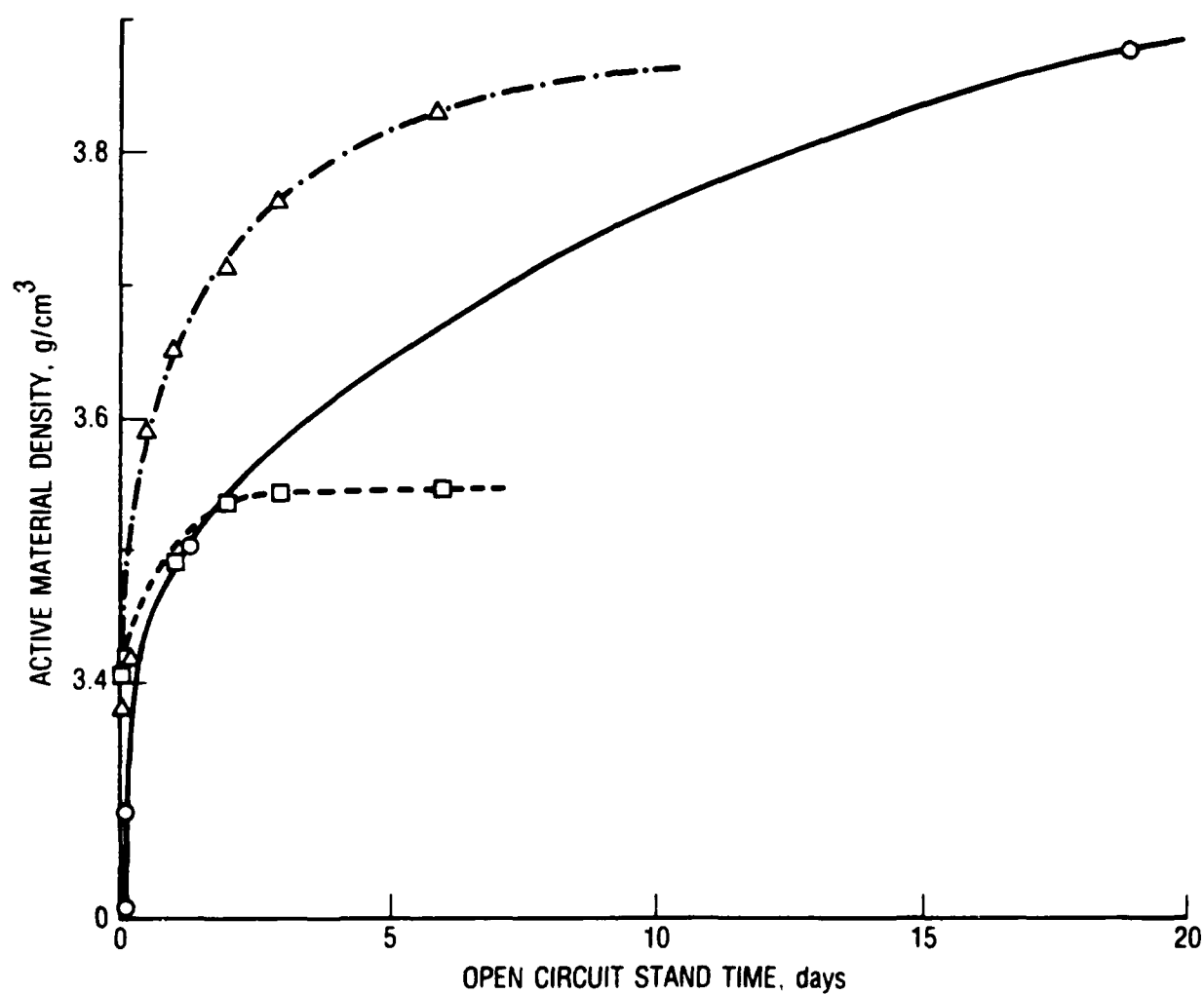


Fig. 2. Change in Density as a Function of Time During Open Circuit Stand in 31% KOH for a Chemistry Impregnated Nickel Hydroxide Electrode. The dash line is for a state of charge of 0.007, the dot-dash line is for a state of charge of 1.365, and the solid line is at a state of charge of 0.169 obtained by discharging from a 1.50 state of charge.

density states to be generated. Conversely, the more highly loaded electrode of Fig. 1 tended to attain lower average states of charge, and is likely to have developed some charge heterogeneity in the active material. After most conditions of operation, the active materials had relaxed to a near steady density condition after 5 to 10 days of open circuit stand. However, when any of the electrodes were overcharged at a C/10 rate for lengthy periods of time, the relaxation of the density during subsequent open circuit stand could continue for many weeks. A similar slow relaxation of the density over many weeks was also observed when the electrodes were discharged following extended overcharge, behavior that is indicated in Fig. 2. This behavior implies that the disordered structures created during extended overcharge are maintained as the electrode is discharged, and that a high density active material can only be regenerated by allowing for a long period of annealing. This behavior is consistent with the formation of γ -NiOOH during extended overcharge, which on discharge is converted to a relatively disordered α -Ni(OH)₂, then relaxes slowly to β -Ni(OH)₂.

The changes in density during open circuit stand, particularly at high states of charge, provide a possible mechanism for increased stress within nickel electrodes during stand periods. These effects are expected to be greatest during charged stand, which is a mode of operation that has been found to enhance degradation in nickel cadmium cell tests⁷. The effects of cobalt additives are indicated in Fig. 3. With cobalt present, it is even clearer that two types of active material having distinct densities are generated. The electrode in Fig. 3 could be cycled at relatively low states of charge while remaining at all times in a high density state at about 3.6 g/cm³. This high density state underwent only minimal changes in density during open circuit stand. Overcharge of the electrode that contained cobalt tended to generate a low density form of the active material that could be converted back to the higher density form by allowing it to stand open-circuited for many days, as is indicated in Fig. 3.

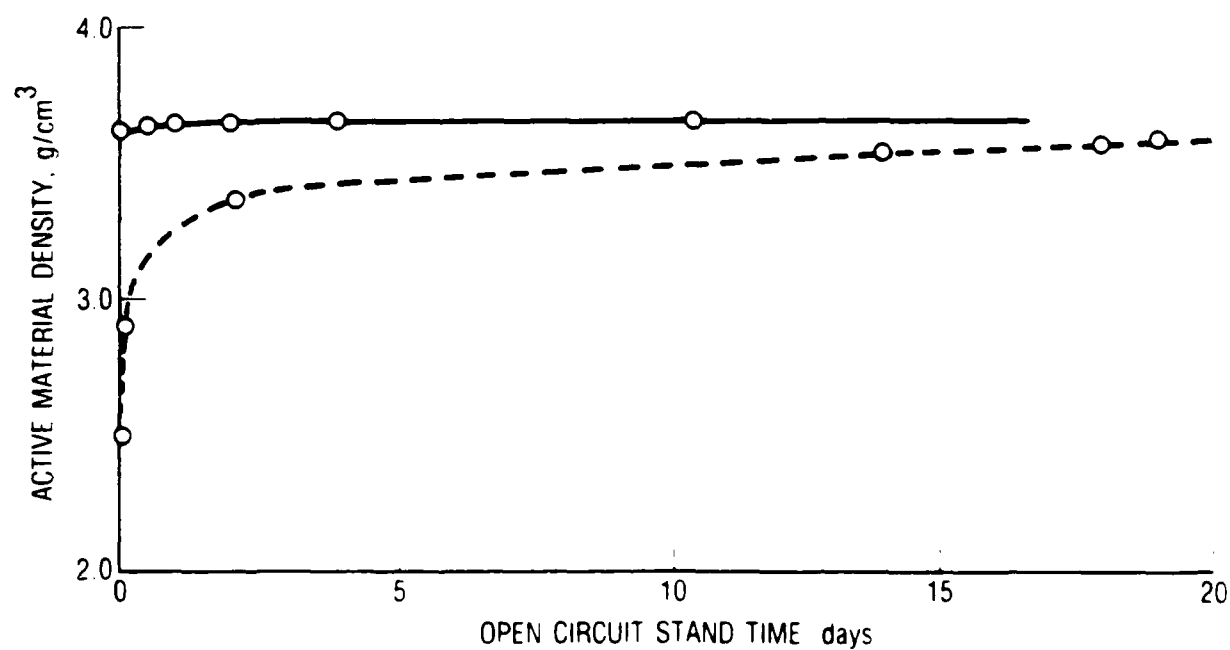


Fig. 3. Change in Density as a Function of Time During Open Circuit Stand in 31% KOH for a Chemically Impregnated Nickel Hydroxide Electrode Containing 10% Cobalt Hydroxide. The solid line is for a state of charge of 0.222 and the dash line is for a state of charge of 1.017.

C. DEPENDENCE OF DENSITY ON STATE OF CHARGE

The kinetics of density relaxation indicated in Figs. 1-3 at different states of charge indicate that significant changes in active material density occur as a function of state of charge. These dependences are more clearly illustrated in Figs. 4-6 by plotting density as a function of state of charge for the three electrode types that were studied. Since the density does change with stand time as indicated in Figs. 1-3, both the initial density and the density value measured after 100 hours of open circuit stand are plotted as a function of state of charge in Figs. 4-6.

For the electrochemically impregnated electrode (Fig. 4), both the initial density and the density after 100 hours of stand were found to increase regularly with state of charge. Increases in the density during stand were about 0.1 g/cm^3 (~ 3%) at all states of charge that were measured (up to 1.02). The electrochemically impregnated electrode exhibited significantly lower utilization of active material than did the other electrodes when charged at the C/10 rate, which is why states of charge of only 1.02 could be reached for this electrode. The low utilization is presumably a result of the higher average loading levels that existed in this electrode.

The changes in density with state of charge for the chemically impregnated nickel hydroxide electrode are indicated in Fig. 5. In contrast to the behavior noted in Fig. 4 for the electrochemically impregnated electrode, the initial density for this electrode exhibited no systematic dependence on state of charge. The density increase measured after 100 hours of stand ranged from about 0.1 g/cm^3 at zero state of charge to about 0.4 g/cm^3 at a state of charge of 1.25. The density after stand rose monotonically with increasing state of charge; however, the slope of the density increase did appear to decrease at a state of charge of about 0.5.

The addition of cobalt additive appears to have a tremendous effect on how the density varies with state of charge, as indicated in Fig. 6. At states of charge below 0.6 to 0.7, the density increases monotonically with state of charge in a manner similar to the behavior of the electrodes containing no

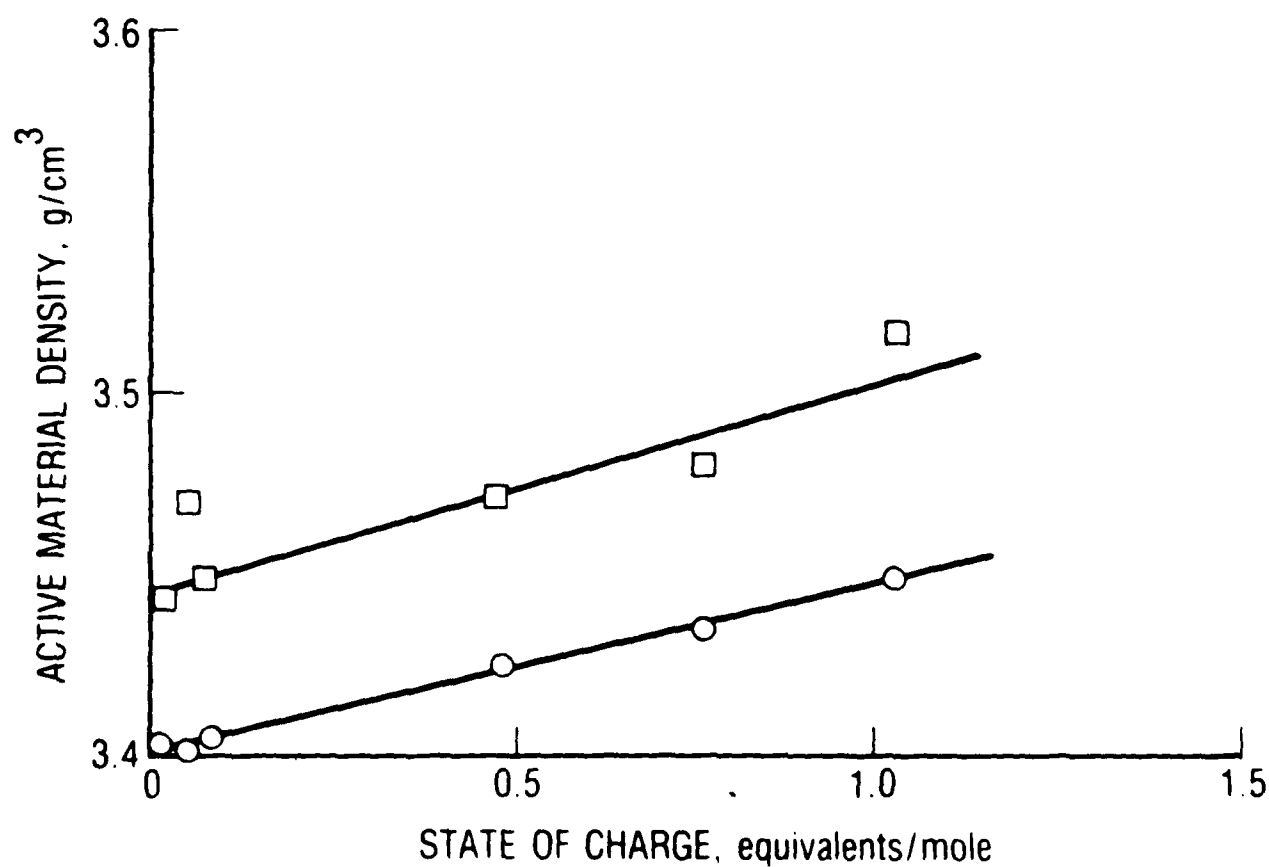


Fig. 4. Change in Density with State of Charge for Electrochemically Impregnated Nickel Electrode. The circles and lower line indicate the density immediately after charging the electrode to the indicated state of charge at the C/10 rate, while the squares and upper line indicate density measurements after 100 hours of open circuit stand in 31% KOH.

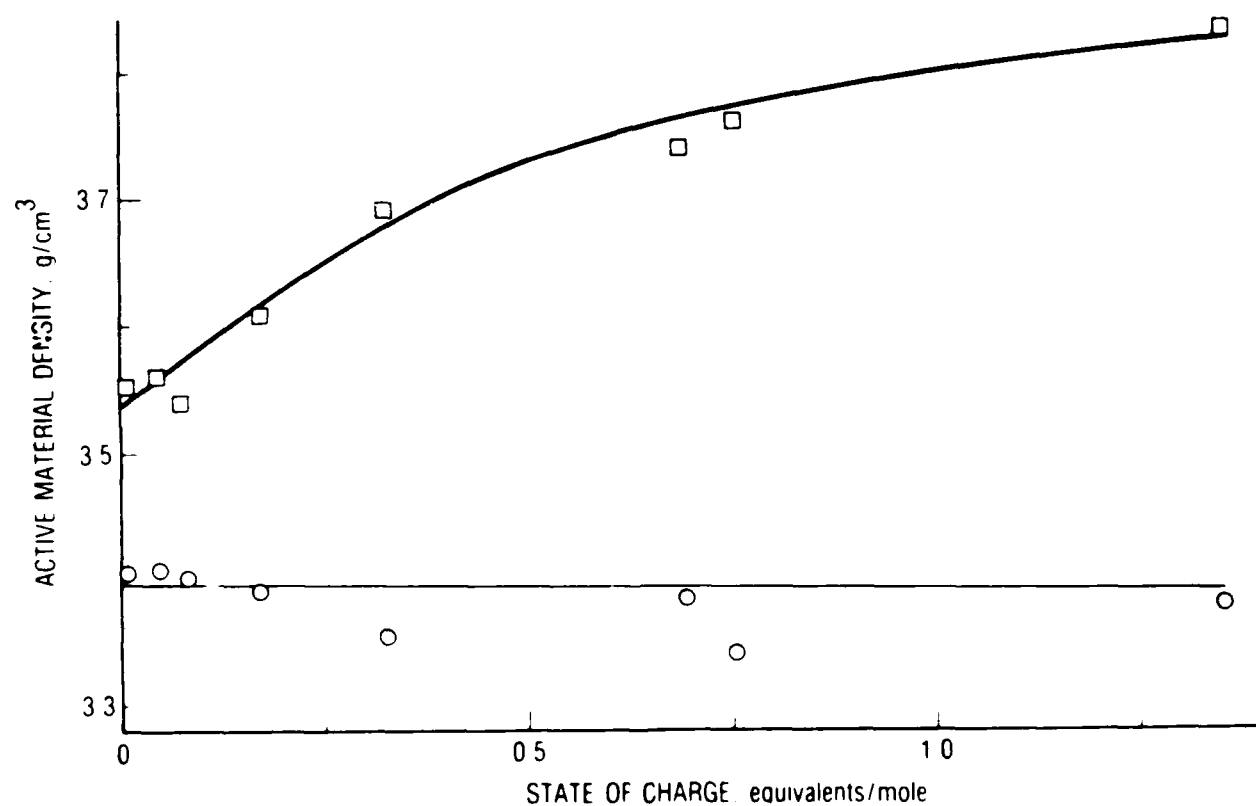


Fig. 5. Change in Density with State of Charge for Chemically Impregnated Nickel Electrode. The circles and lower line indicate the density immediately after charging the electrode to the indicated state of charge at the C/10 rate, while the squares and upper line indicate density measurements after 100 hours of open circuit stand in 31% KOH.

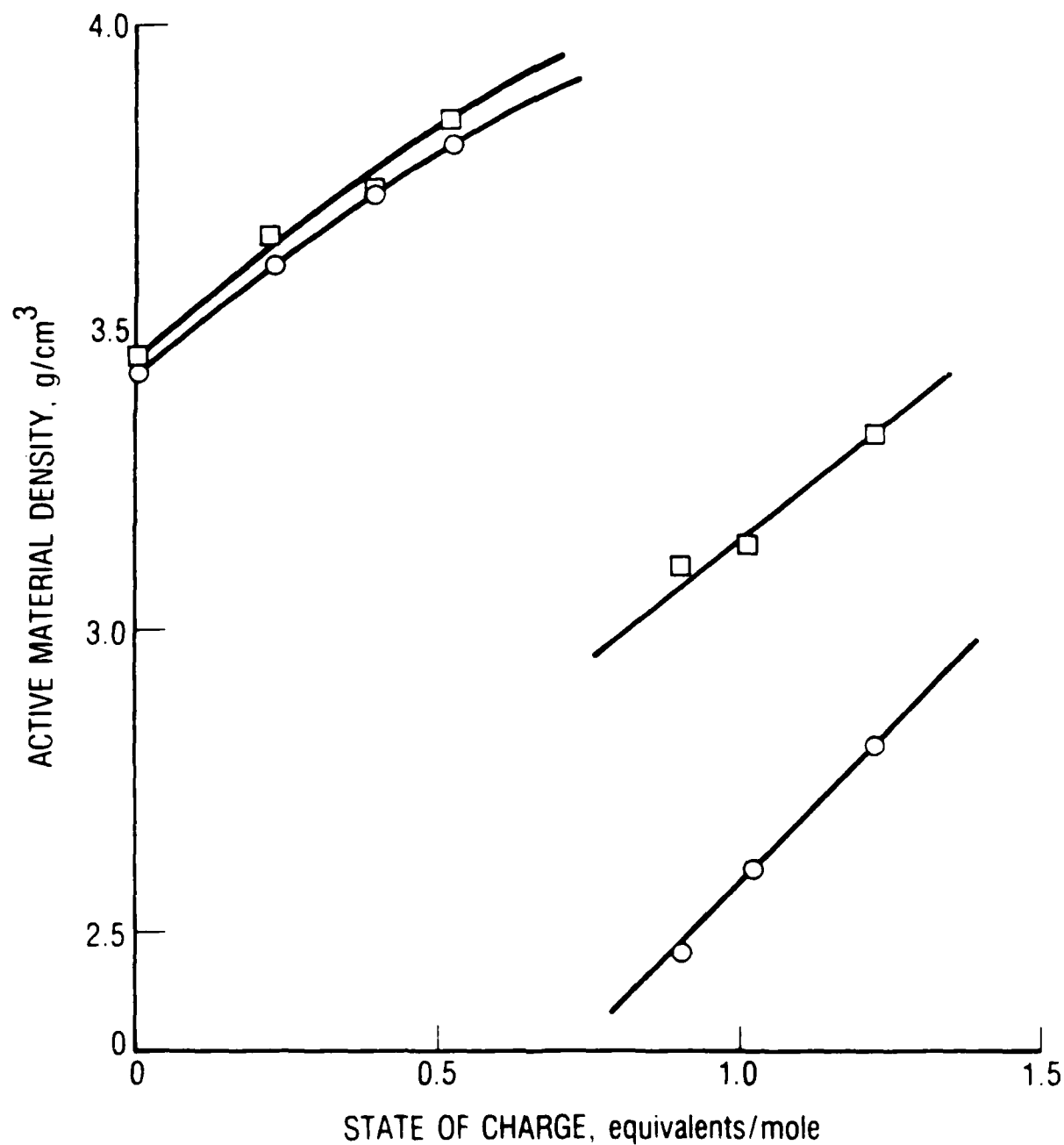


Fig. 6. Change in Density with State of Charge for Chemically Impregnated Nickel Electrode Containing 10% Cobalt Hydroxide. The circles indicate the Density Immediately after charging the electrode to the indicated state of charge at the C/10 rate, while the squares indicate density measurements after 100 hours of open circuit stand in 31% KOH.

cobalt additive. Only small changes in density were observed during open circuit stand for the electrode containing cobalt at low states of charge. At states of charge above 0.8, the density of the active material immediately after electrochemical activity decreased dramatically, typically attaining values in the range of 2.4 to 3.0 g/cm³. The density at the states of charge above 0.8 increased from these low values towards the higher density range (above 3.5 g/cm³) with extended open circuit stand, as is indicated in Fig. 3.

The variations of active material density with state of charge indicated in Fig. 6 appear to be consistent with a phase transformation taking place above 0.7 state of charge. The significant decrease in density indicates that disorder has resulted, either from changes in lattice structure or from microscopic movement of the active material crystallites. Large changes in density were not observed near 0.7 state of charge when cobalt was not present, as indicated in Figs. 4-5. This suggests that either the phase transition does not occur without cobalt present, or weight and volume changes associated with the phase transition may cancel each other when no cobalt is present. The voltage changes that accompany this shift in active material density are indicated in Fig. 7 for the electrode with cobalt additive. The density changes begin to occur when the nickel electrode voltage starts to swing up prior to the voltage peak that generally indicates when full charge is reached. Since previous work⁸ has indicated that this voltage peak can occur at times when charge efficiency is essentially 100%, it is attractive to identify the voltage peak as being caused by the overpotential required to cause a phase transformation in the active material. This may be a β -NiOOH phase that has been identified in the work of Barnard^{4,11} as being formed during charging of nickel oxyhydroxides to states of charge between 0.75 and 1.00. It is clear that cobalt can have a major impact on the lattice changes occurring in the nickel oxyhydroxide material as the voltage increases into the oxygen evolution region.

As indicated in the preceding paragraph, the density changes in Figs. 4-6 can be composed of a combination of changes in the active material mass (as indicated by changes in its dry weight) and changes in the specific volume. If a γ -NiOOH phase is being formed as the electrode goes into overcharge,

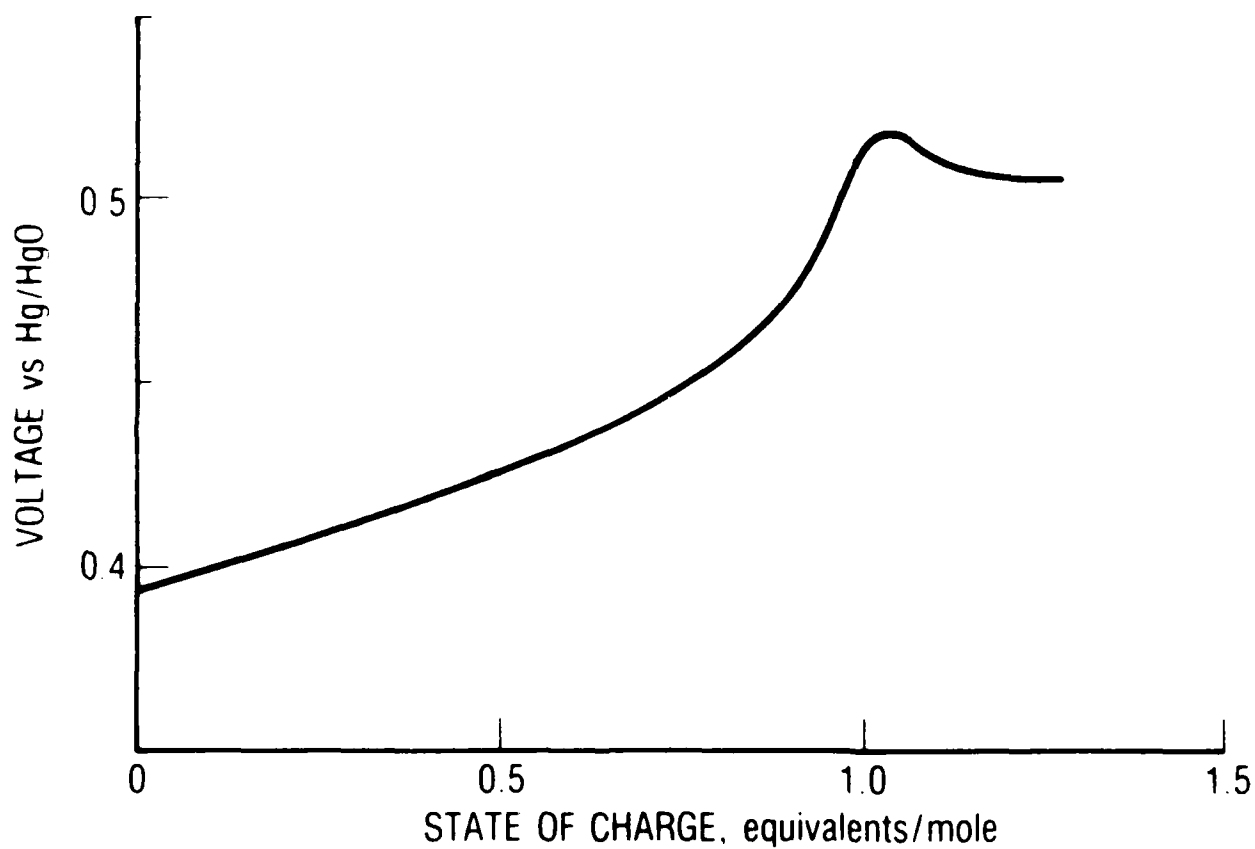


Fig. 7. Voltage as a Function of State of Charge for Chemically Impregnated Nickel Electrode Containing 10% Cobalt Hydroxide During Recharge at 2 ma/cm^2 (C/10 rate). The voltage has been compensated for IR drop in the electrolyte.

work done by Barnard⁹ indicates that a mass increase should be observed due to incorporation of potassium ions into the active material structure. A plot of active material weight as a function of state of charge is indicated in Fig. 8 for the three electrodes tested here. Figure 8 indicates that the active material in all the electrodes exhibited a significant weight increase as they approached a state of charge of 1.0. The weight increase for the electrode with cobalt additive, which showed large density changes at states of charge from 0.7 to 0.8, only begins to show significant change in active material weight after the voltage peak in Fig. 7 (at a state of charge of about 1.0) is passed. Since the density for this electrode shows a marked decrease well before this peak is reached, it is likely that the incorporation of significant amounts of potassium into the lattice is not required to cause the reduction in density. The data in Fig. 8 appear to be consistent with macroscopic disorder being created in the active material as the voltage begins to swing up and oxygen evolution begins at higher states of charge. Figure 8 also suggests that continued charging results in a weight pickup that is likely to be caused by the pickup of potassium ions from the electrolyte. The slow increase in the density of the electrode in Fig. 2, after being brought to a high state of charge and then discharged, may involve a slow macroscopic reordering of the active material crystallites as the potassium ions remaining in the structure are gradually removed.

The changes in the volume of the active material within the pores of the sintered electrodes are expected to be an important element in determining the stress levels to which the sinter structure is subjected during electrode operation. This has been pointed out in work done by Fritts.¹ The changes in volume that accompany the density changes measured here are indicated in Figs. 9 and 10 for the three electrode types. The volume plotted was that measured after 100 hours of open circuit stand. The volumes that were measured with no stand time were generally somewhat greater than at 100 hours; however, the dependence on state of charge was similar. These data clearly show that the active material volume decreases as the state of charge increases over the range of 0.0-0.7. In this range the volume decrease varies from 8.5% for the heavily loaded (electrochemically) nickel hydroxide electrode, to about 16%

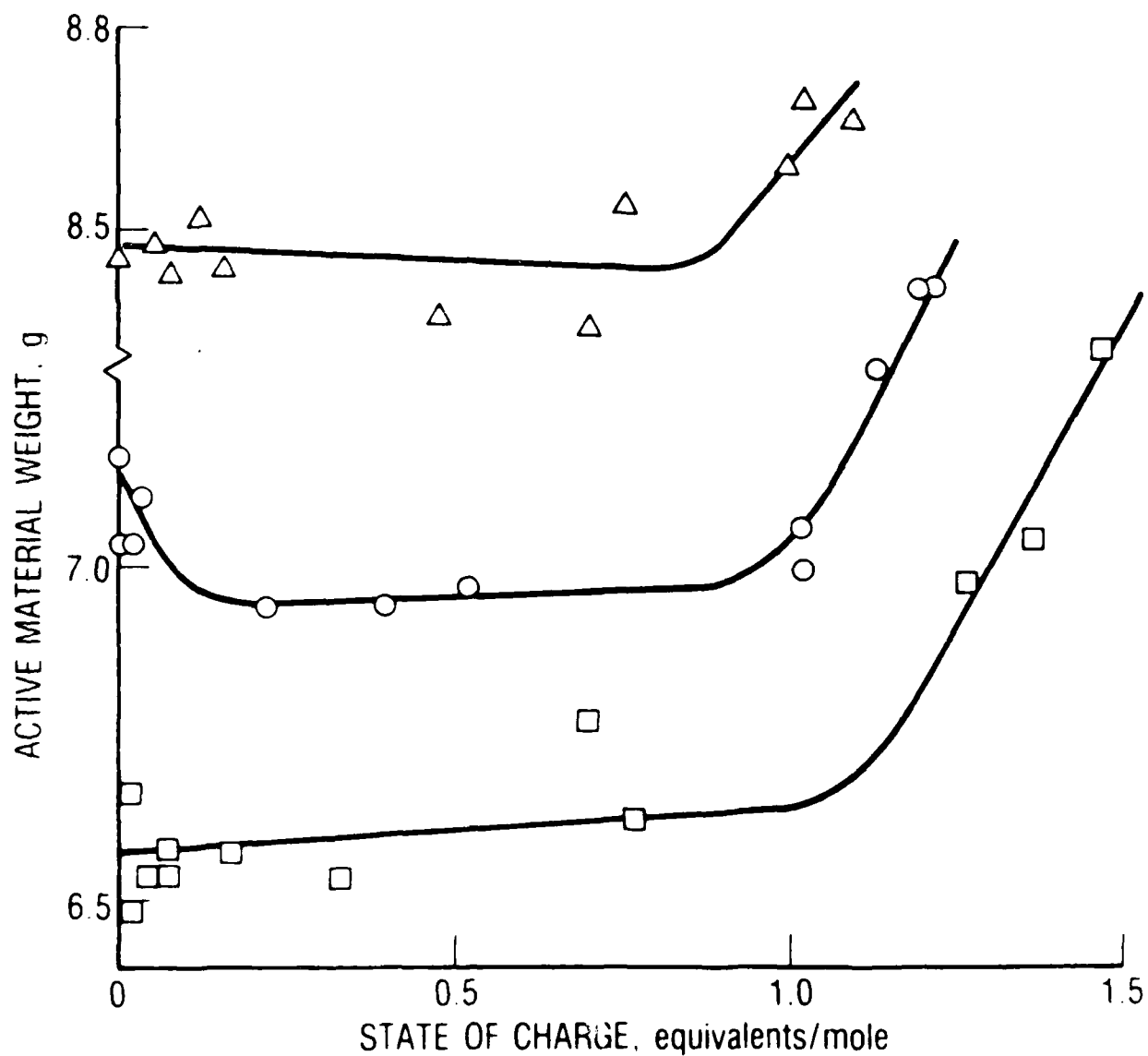


Fig. 8. Weight of the Active Material in the Nickel Electrodes Studied as a Function of State of Charge. The squares and lower line are for the chemically impregnated nickel electrode, the circles and middle line are for the chemically impregnated nickel electrode containing 10% cobalt additive, and the triangles and upper line are for the electrochemically impregnated nickel electrode.

for the electrode containing 10% cobalt. This decrease in volume is expected to accompany the oxidation of $\beta\text{-Ni(OH)}_2$ to $\beta\text{-NiOOH}$, which has been suggested by Barnard⁸ to occur up to states of charge of 0.75 before the formation of other phases of active material begin.

All the electrodes undergo an abrupt increase in active material volume at a state of charge of about 0.7, as shown in Figs. 9 and 10. This abrupt volume increase was 8-9% for the electrodes with no cobalt, and about 31% for the electrode containing 10% cobalt in the active material. The electrode containing cobalt, when prepared in this high volume state, showed a very slow decrease in volume if allowed to stand, although many weeks were generally required before a low volume condition was again attained. After the abrupt change in active material volume at about 0.7 state of charge, the volume changes were not extremely large and tended to be somewhat variable as state of charge was further increased. The abrupt change in volume at about 0.7 state of charge is again consistent with the initiation of macroscopic disorder caused by oxygen evolution, which can precede the formation of the $\gamma\text{-NiOOH}$ phase of the active material. These results suggest that physical transformation of the active material structure can occur at states of charge that are quite low compared to the full charge point reached during electrode operation in battery cells.

D. ACTIVE MATERIAL COMPRESSIBILITY

Since changes in active material volume are expected to contribute to the stresses within the sintered electrode structure, it is somewhat surprising that electrodes with cobalt added exhibit such large changes in volume (Fig. 10). Cobalt has been found in the work of Fritts¹ to significantly reduce stress on the sinter structure. Fritts determined that this resulted from increased elasticity of the active material rather than changes in volume. These observations suggest that under normal conditions of electrode operation, which do not generally involve long periods of open circuit stand, the active material remains in the low density or high volume state at all times. While under some conditions of discharge this low density state may not thermodynamically be the most stable configuration, insufficient time is

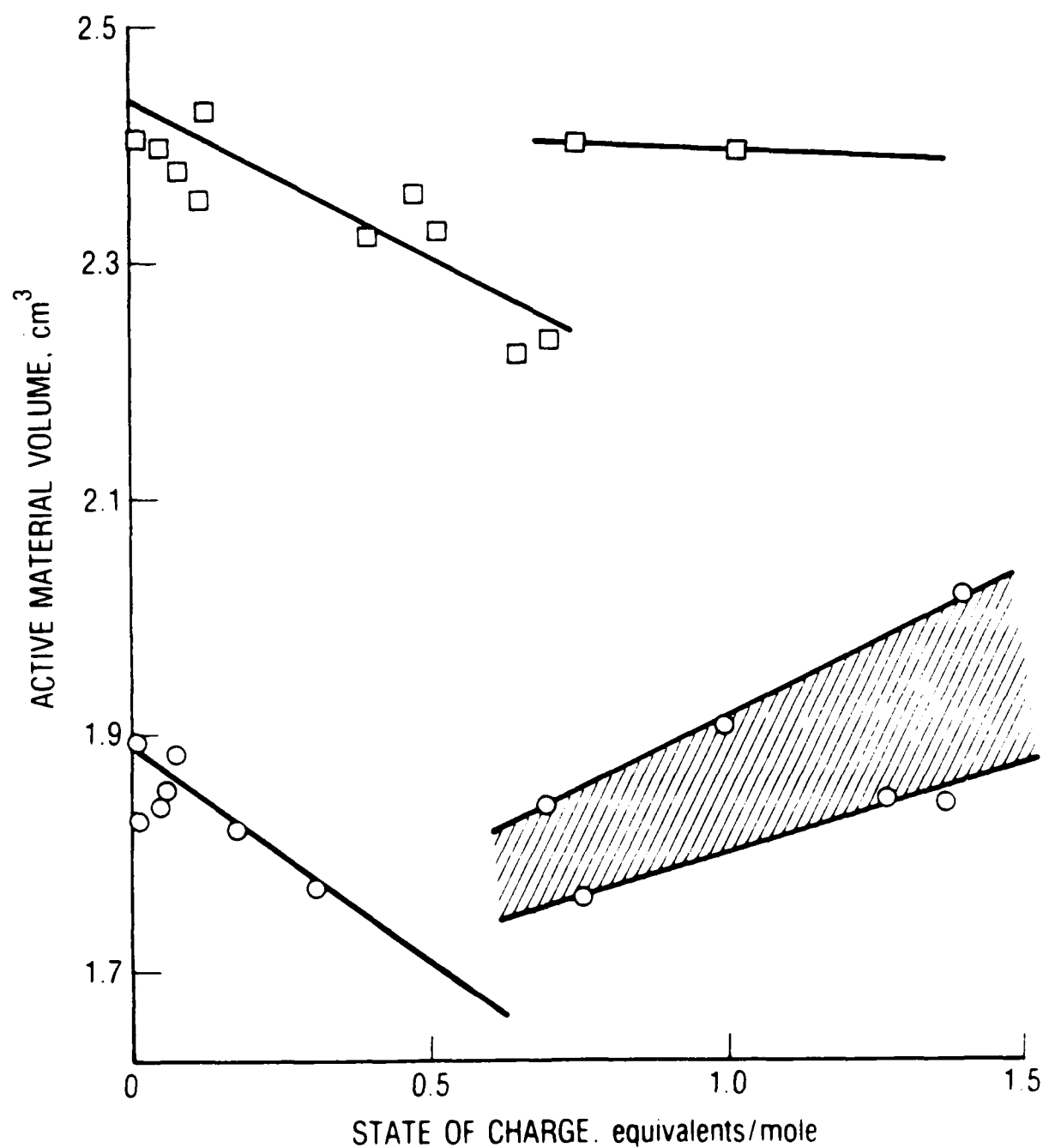


Fig. 9. Volume of the Active Material in the Nickel Electrodes Containing Pure Nickel Oxyhydroxides as a Function of State of Charge. The circles at lower volumes indicate measurements for the chemically impregnated electrode, while the squares at higher volumes indicate measurements for the electrochemically impregnated electrode.

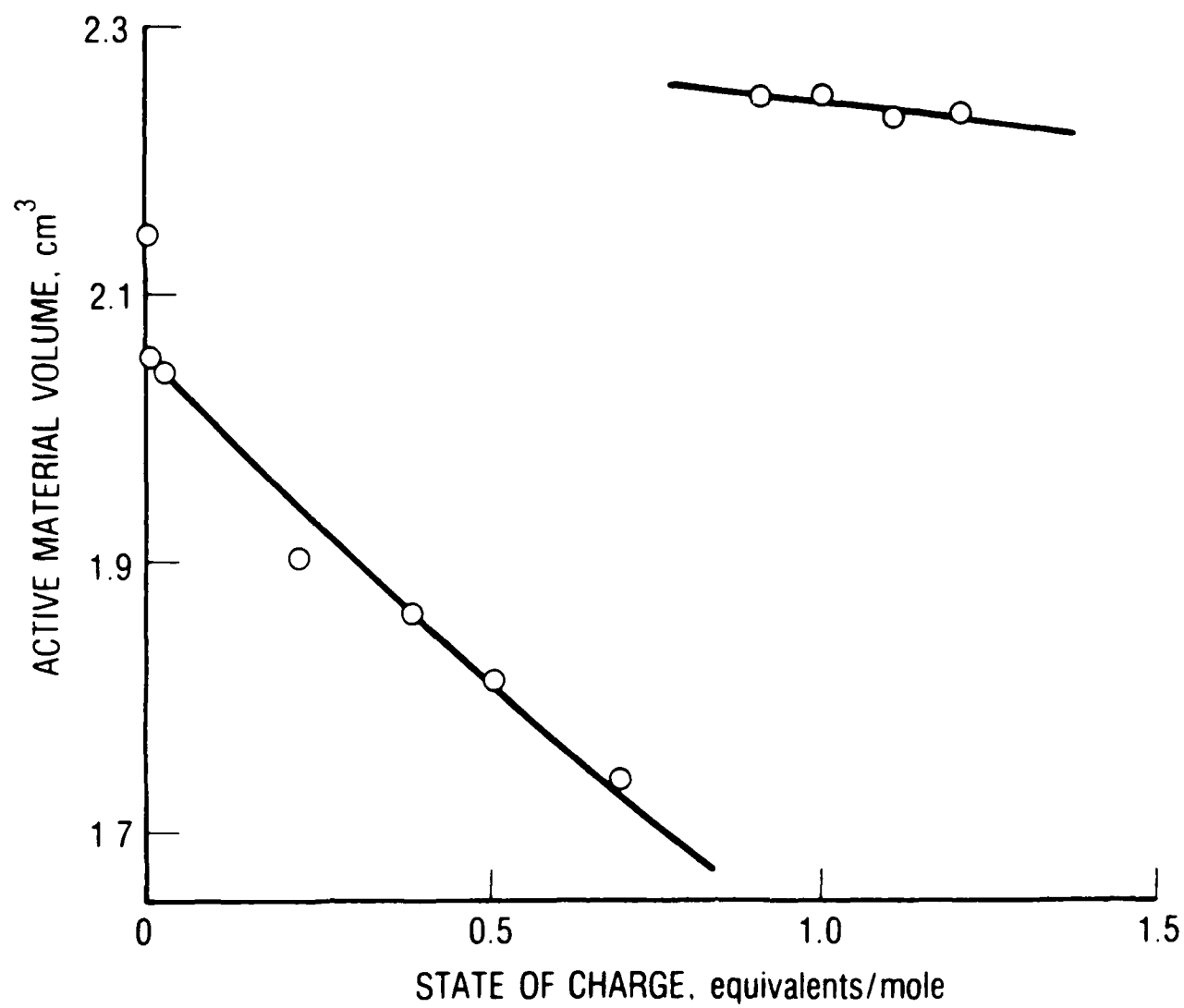


Fig. 10. Volume of the Active Material in the Nickel Electrode Containing 10% Cobalt as a Function of State of Charge

generally spent under these conditions for the electrode to relax. Changes in elasticity, which would be exhibited as changes in active material compressibility in the measurements done in this study, could then act as a dominant factor in absorbing stresses arising from active material expansion and contraction, and thus causing less stress to be exerted on the sinter structure. To determine whether this picture is consistent with the data reported here, the compressibility of the active material was measured over a range of operating conditions and states of charge.

The compressibility of the active material was measured for the electrodes in this study by monitoring the change in density in response to a 14.7 psi pressure change. This method allowed compressibilities to be measured to a precision of about $\pm 0.002\%$ /psi, an uncertainty that also established a lower limit of detection for the compressibility. The compressibility for all the electrodes was found to be a strong function of active material density. For densities of about 3.4 g/cc or greater, the compressibility was typically less than 0.01%/psi, often being less than the lower detection limit of 0.002%/psi. As indicated in Fig. 11, the electrodes containing no cobalt gave a compressibility less than 0.025%/psi for all conditions of electrode operation studied here. The highest compressibilities were measured in the charged state immediately after the electrodes were brought to full charge.

The electrode that contained cobalt additive exhibited compressibilities as high as 1%/psi for measurements made just after the electrode had been brought to a high state of charge. The dependence of compressibility on state of charge is illustrated in Fig. 11 for this electrode. The compressibility remains very low until states of charge of 0.7-0.8 are reached, after which it begins to increase sharply with increasing state of charge, particularly for the electrode containing cobalt. While the compressibility also increases in this high state of charge region for the electrodes without cobalt, the increase is approximately 40 times less than for the electrode containing 10% cobalt. It should again be pointed out that the low density, high compressibility states formed by electrochemically driving the active material to a high state of charge are maintained for significant periods of time

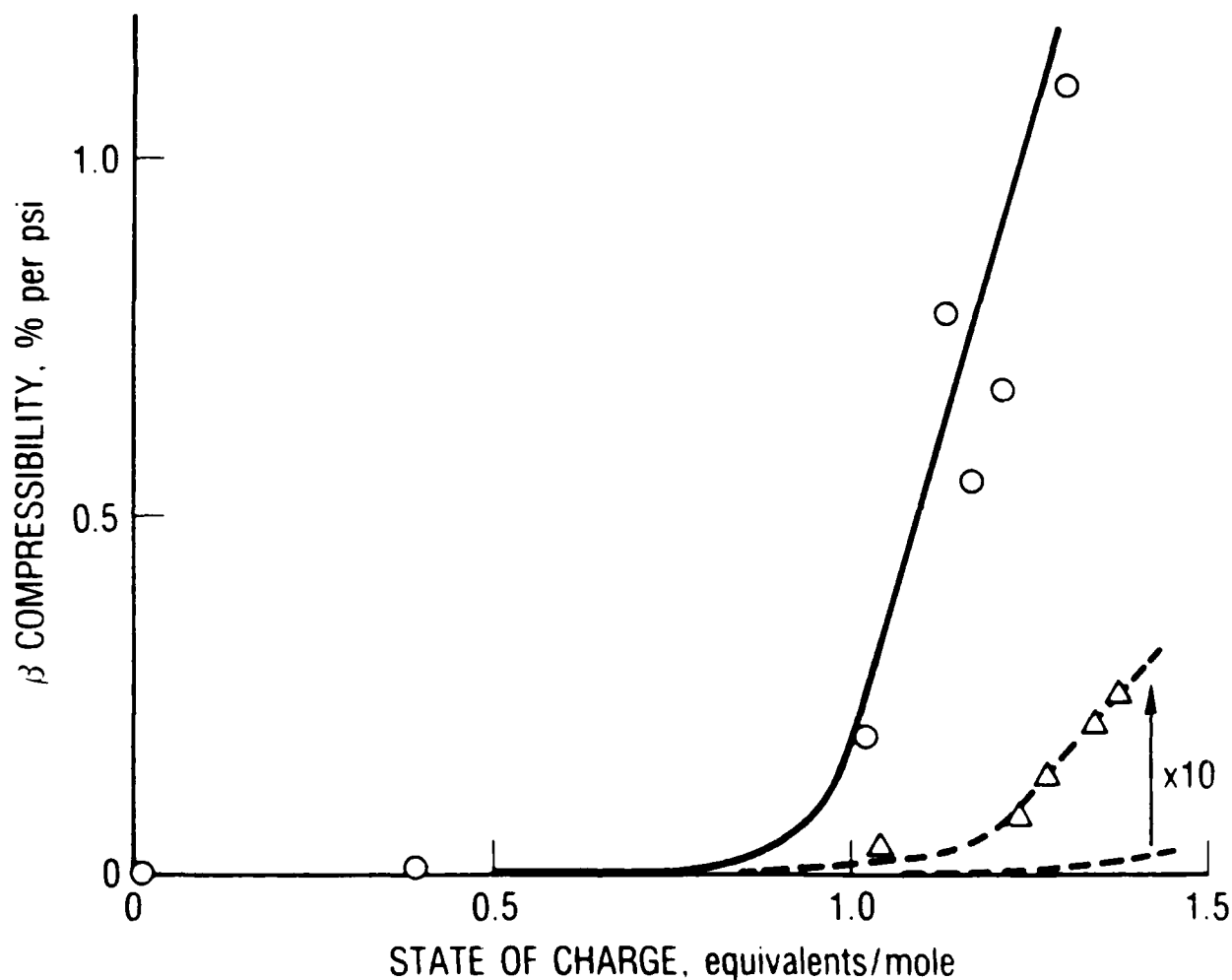


Fig. 11. Compressibility of the Active Material in Chemically Impregnated Nickel Electrodes as a Function of State of Charge. The circles correspond to compressibility measurements for the electrode containing 10% cobalt additive, the dashed lines indicate the compressibility of the active material consisting of pure nickel oxyhydroxide. The triangles indicate the compressibility for the pure active materials multiplied by 10.

(days) even after discharging to lower states of charge. The compressibility of the low density states formed at high states of charge increases by nearly two orders of magnitude by the addition of 10% cobalt to the active material. This is the same order of magnitude that the internal stresses were found to be reduced in Ref. 1 by the addition of about 10% cobalt to the active material in sintered electrodes. These results are therefore consistent with cobalt additives decreasing the stress levels in nickel electrodes by causing an increase in the compressibility of the active material.

The electrode containing cobalt exhibited a wide range of compressibilities, depending on the density of the active material and the conditions of charge or discharge to which the electrode had been exposed. The relationship that was observed between active material compressibility and density for this electrode is indicated in Fig. 12. The upper line is drawn through points corresponding to measurements taken after a day or more of open circuit stand to allow some equilibration to take place. The lower line is drawn through points corresponding to measurements taken during the first 10 hours of open circuit stand following charge or discharge. The lower line is likely to reflect different characteristics because the active material is continuing to undergo deformation and movement in response to the stresses of charge or discharge during the hours immediately following such electrical activity. Such structural relaxation may occur both at the microscopic level, involving changes in the lattice and defect structure, and at the macroscopic level, involving movement and deformation of active material crystallites.

E. EFFECTS OF CYCLING

Nickel electrodes containing cobalt additive are often used in nickel cadmium or nickel hydrogen batteries in a continuous cycling mode of operation that would not involve significant periods of time on open circuit or trickle charge. Such usage generally returns the nickel electrodes to a high state of charge on each cycle, and therefore would be expected to maintain the active material in the low density state. While some cyclic changes in active material density are possible due to the active material becoming more dense when it is discharged to states of charge less than about 0.7, these density

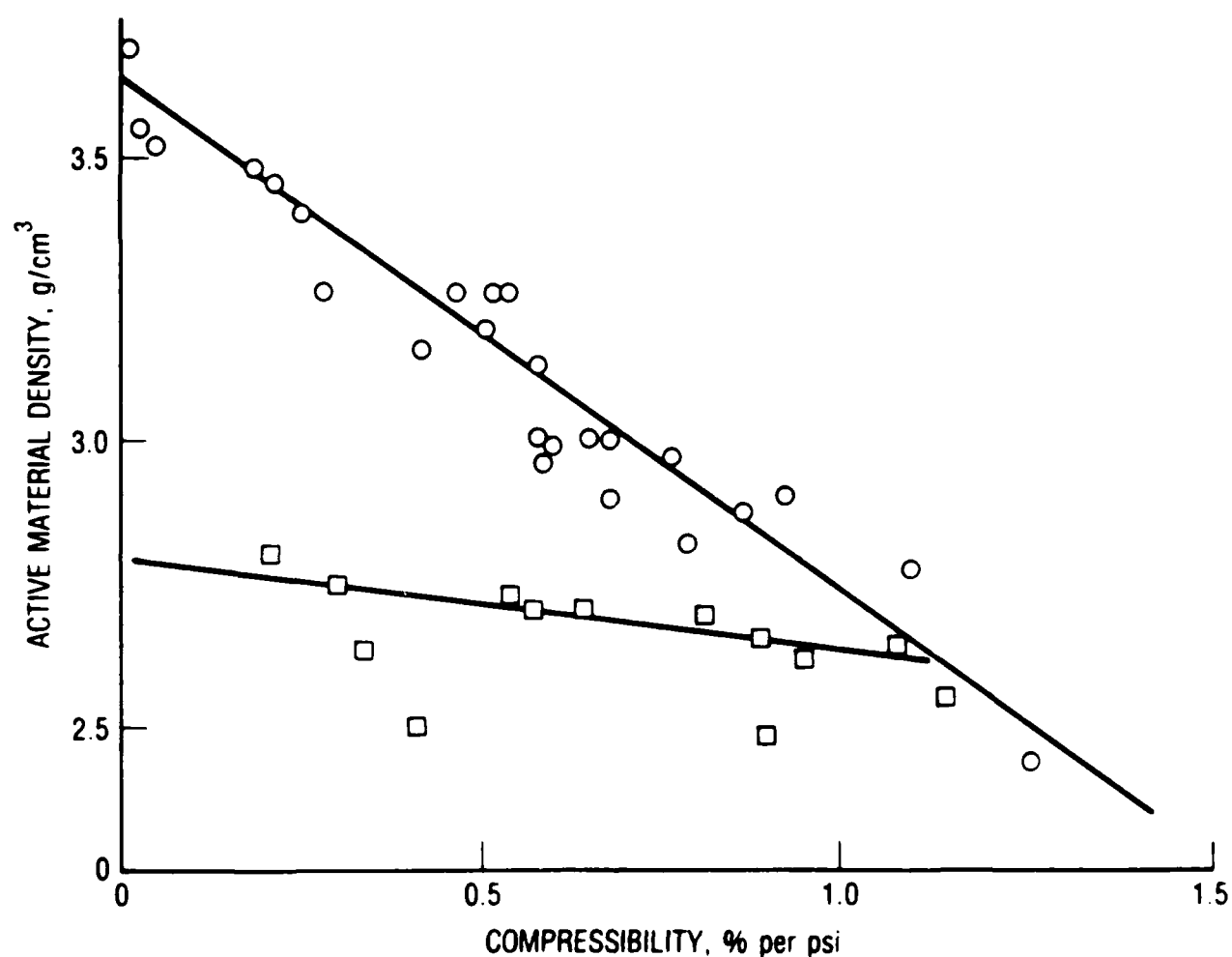


Fig. 12. Density of Nickel Active Material as a Function of Compressibility for Electrode Containing 10% Cobalt Additive. The lower line is drawn through points measured within 12 hours after electrochemical activity, while the upper line is drawn through points measured after at least 24 hours of open circuit stand in 31% electrolyte.

changes will not be large unless significant time is spent at the lower states of charge. For low earth orbit battery applications, which involve relatively rapid discharge and recharge, very little stress from density changes may be encountered as long as depth of discharge does not exceed 20-25%. At depths of discharge less than 25%, the state of charge never decreases below about 0.7, therefore remaining in a region where low density, high compressibility behavior is consistently observed. Test data for nickel cadmium cells are consistent with significantly improved performance at low depths of discharge in low earth orbit tests.¹⁰

A continuous cycling test was run on the chemically impregnated electrodes containing pure nickel hydroxide and 10% cobalt additive. This test involved operating the electrodes for 24 cycles, each cycle consisting of charge at 2 ma/cm² (C/10) until 115% of the charge removed during the previous discharge was returned, then discharge at 10 ma/cm² (C/2) to 0.2 volts vs. Hg/HgO. After these cycles were completed, the fully charged electrode (state of charge was greater than 1.0) was allowed to stand open circuited while the active material density was monitored over a 100-hour period. The electrode with cobalt had active material with a density initially 2.46 g/cm³. The density increased with time and after 100 hours was 3.35 g/cm³ and still gradually increasing. For the electrode without cobalt, the density was similar to that indicated for the fully charged electrode in Fig. 2, being initially about 3.38 and increasing to 3.66 g/cm³ after 100 hours.

These results also suggest that nickel electrode performance changes during cycling may be much different if the electrode is cycled at states of charge that do not exceed 0.7. In this situation, no overcharge would occur and the physical changes that are observed to decrease density at a state of charge of about 0.7 would be avoided. The active material would always exist in the high density state. This condition of operation could reduce stresses arising from volume changes of the active material. However, because compressibility is also reduced by operating in a lower state of charge range, the reduction in stress levels that can be realized by such operation is likely to be limited.

F. EFFECTS OF TRICKLE CHARGE

Stand periods during the use of nickel electrodes in batteries are typically in the fully charged condition and generally employ a low trickle charge current to hold the battery at a high state of charge. The changes in active material density during such trickle charging can affect the stresses on active material in sintered electrodes. The density was measured for the chemically impregnated electrodes, both with and without cobalt additive, as a function of time on open circuit following a 16 hour charge at C/10 (2 ma/cm^2) and a 100-hour trickle charge at C/100 (0.2 ma/cm^2). For the electrode containing no cobalt, the state of charge was greater than 1.27 and the density was 3.55 g/cm^3 immediately after the 100 hours of trickle charge. After 100 hours of open circuit stand, the density had increased to 3.79 g/cm^3 . Comparing these results to the data in Fig. 5 suggests that the density with no cobalt present does increase significantly during C/100 trickle charge, although the density increase during trickle charge is not as great as that during open circuit stand. For the electrode containing cobalt, which had a state of charge greater than 1.17 after trickle charging, the density right after trickle charging was about 3.00 and after 100 hours of open circuit stand was 3.50 g/cm^3 . Comparing these results with the data of Fig. 6, it appears that some density increase occurred during the trickle charge, although at a much lower rate than during open circuit stand.

These results indicate that during trickle charge at C/100, the density of the active material can slowly increase, although at rates much slower than during open circuit. It is likely that such changes in density with time while at full charge occur at rates that are highly dependent on the overcharge current. Such effects may contribute to the lower rates of degradation that have been observed for NiCd cells when trickle charging is used, rather than open circuit for charged stand periods.⁷

IV. DISCUSSION

The results presented in the previous sections indicate that electrochemical cycling of nickel electrode active materials can have a significant effect on the density and molar volume of such materials. The most pronounced changes in volume were found to occur when the oxidation state of the nickel exceeded about 2.75 (0.75 state of charge). Work by Barnard et al.¹¹ has indicated that at nickel oxidation states above about 2.75 a change in active material structure (or phase) begins to occur, and involves the formation of phases having a higher nickel oxidation state. The oxidation state where such higher valency materials are formed is thus consistent with the state of charge where pronounced decreases in density and increases in molar volume were observed in this work. The onset of such a phase transition could contribute to the significant volume change seen here at states of charge of about 0.75. However, it also appears likely that the onset of oxygen evolution also occurs in this state of charge range, and could provide a significant source for the large increase in the apparent molar volume. The molar volume in this case would include the volume of gas entrapped in the microstructure of the active material, and which could not be drawn out by vacuum. The high compressibilities observed are consistent with the presence of gas entrapped in the active material.

Large changes in the molar volume are generally expected to put stress on the active material deposits and the sinter structure, and act as a driving force to physically move active material within the pores of a sintered electrode. The results obtained here therefore suggest that stable electrode operation is likely to be maintained either by cycling continuously at a high average state of charge (which maintains the active material in a low density state) or by cycling without going to high states of charge (maintains active material in a high density state). Changes in nickel electrode operation from one of these operating modes to the other, such as during reconditioning, storage, extended overcharge, or open circuit, can have a significant effect on the active material density, structure, and electrochemical performance.

Such changes may be either beneficial or harmful to performance, depending on the previous history of electrode performance and cycling operation.

Cobalt additives have been observed to significantly affect the nickel electrode active material density characteristics. The low density form of active material is stabilized with 10% cobalt present to such an extent that the high density material can only be formed by lengthy annealing periods of limited electrochemical activity. Such an effect is likely to stabilize and improve performance in operation involving continuous cycling from a fully charged state. The cobalt also appears to increase the compressibility (softness) of the active material, which should result in improved capability to absorb stresses due to volume changes. However, during long periods of inactivity or storage, active material containing cobalt may exhibit physical changes due to large density increases, followed by large volume increases when recharged. Such physical changes could have a significant effect on performance when cycling is restarted, and are likely to best be reversed by continuous cycling from full charge without allowing lengthy discharged or open circuit periods.

V. CONCLUSIONS

The changes that occur in the density of nickel active materials have been measured and have been found to exhibit significant variations as the conditions of nickel electrode operation are changed. The results show the effects of a phase transition taking place at an oxidation state of about 2.7, which leads to major changes in volume, density, and compressibility of the active material. These effects are particularly pronounced when cobalt additives are present in the active material. It was also observed that recovery of the density after such a phase transition could be quite slow, requiring several days. Time constants of this kind for physical changes in the nickel electrode may be a primary cause for observations often made that nickel electrode performance can be affected significantly by its prior operating history. These results suggest some possible ways to influence nickel electrode life and operating characteristics by varying how charge is managed or storage is done.

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LABORATORY OPERATIONS

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Aerophysics Laboratory: Launch vehicle and reentry fluid mechanics, heat transfer and flight dynamics; chemical and electric propulsion, propellant chemistry, chemical dynamics, environmental chemistry, trace detection; spacecraft structural mechanics, contamination, thermal and structural control; high temperature thermomechanics, gas kinetics and radiation; cw and pulsed chemical and excimer laser development including chemical kinetics, spectroscopy, optical resonators, beam control, atmospheric propagation, laser effects and countermeasures.

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