Mechanisms for Capacity Fading in the NIH$_2$ Cell and its Effects on Cycle Life

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During recent years there have been a number of instances where the capacity of nickel hydrogen battery cells has proven to be unstable during storage. The capacity losses seen after periods of cell or battery storage have typically varied from only a small amount of fading, up to about 30% of the total cell capacity. Detailed studies into the root causes for such fading have been carried out in a number of instances. This report provides an overview of the different mechanisms that have been found to be responsible for such capacity fading in nickel hydrogen cells, and summarizes the presently available data on how each responsible mechanism affects ultimate cell cycle life.

A clear result from the observations of capacity fading and the analyses that have been done for each case, is that there are a number of factors that can either cause or accelerate fading. In general, the origins of capacity fading may be linked to the presence of the highly catalytic platinum material in the hydrogen electrode. This high catalytic activity enables the other components in the nickel hydrogen cell, primarily the nickel electrode, to undergo chemical changes into thermodynamically more stable materials via pathways not otherwise readily available. Unfortunately, in general the chemical modifications that result from such processes tend to degrade rather than enhance cell performance. During the past 10 years, nickel hydrogen cell fading has been observed to result from chemical or physical changes in the electrodes, separator, and electrolyte during storage.

The discussion of capacity fading in nickel hydrogen cells is divided here into two general sections. The first section describes mechanisms for capacity fading in hydrogen precharged cells. This mechanism is relatively well understood through a number of studies published over recent years (Refs. 1-3). Fading in hydrogen precharged cells is controlled by chemical changes that take place in the nickel electrode. The second section discusses capacity fading mechanisms in nickel precharged cells. Such fading is clearly slower than that in hydrogen precharged cells, and can be caused by either temporary or permanent loss of the nickel precharge, or by leaking of hydrogen. The loss of nickel precharge can be induced by chemical changes in the nickel hydrogen cell, or by changes in the electrochemical activity of the nickel electrode.

Fading in Hydrogen Precharged Cells

The balance between the capacity in the nickel electrode and that in the hydrogen electrode in a hydrogen precharged nickel hydrogen cell is graphically illustrated in Fig. 1. The cell

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is built with sufficient hydrogen gas to leave some hydrogen remaining in the fully discharged cell. In this case the cell capacity is always limited by the active capacity of the nickel electrode, assuming that no significant leaks exist in the cell pressure vessel. Typically the nickel electrode delivers approximately 70-80% of its total capacity at useful discharge rates. The remaining capacity is divided into residual capacity, i.e. capacity that can be discharged at reduced rates and voltages, and unavailable capacity, which simply cannot be electrochemically discharged. The relative proportions of residual and unavailable capacity can vary depending on the construction details of the nickel electrode and how it is charged and discharged. However, the residual capacity is often about 20% of the cell capacity and the unavailable capacity is about 5% of the total.

Thus, during the storage of a nickel hydrogen cell with hydrogen precharge in a fully discharged state, the presence of remaining hydrogen gas forces the nickel electrode to the highly reducing potential of the hydrogen electrode. Indeed, under these conditions the nickel electrode becomes a hydrogen electrode having an appreciable reducing capability. This occurs as the compact oxide layers on the nickel sinter are reduced, thus de-passivating the catalytic nickel metal surfaces. Since both the nickel and the platinum electrodes act as hydrogen electrodes, the potential of the cell during storage is clamped very close to zero volts -- irrespective of whether the cell is left open circuited or is shorted.

The reducing environment at the nickel metal surfaces during storage initiates reduction of the nickel and cobalt hydroxides (cobalt hydroxides are generally added to the nickel electrode active material at levels of 5-10% to improve performance and life) if the cell potential is below 0.1 volts, which is guaranteed by the presence of excess hydrogen. These reduction reactions produce finely divided nickel and cobalt metal in the layers that are in electrical contact with the nickel current collecting surfaces within the sinter of the electrode. This solid state reduction process propagates slowly into the active material deposit during lengthy storage periods. Subsequent recharge of the cell will oxidize these metallic particles to the respective nickel and cobalt hydroxides. As described in Ref. 1, cobalt hydroxide thus formed is soluble to some extent in alkaline electrolyte, forming the dicobaltite ion, $HCoO_2^-$. Movement of this ion results in migration of cobalt away from the nickel surfaces. The cobalt is redeposited in any of a number of inactive cobalt containing phases, including $CoOOH$, $CoHO_2$, and Co_3O_4 during subsequent cell operation. Capacity fading can result from layers of these poorly conducting materials preventing discharge of some active material, or probably more likely, preferential discharge of the cobalt-depleted layer surrounding all the current collecting surfaces. Such preferential discharge will occur because cobalt depleted nickel hydroxide has an elevated discharge voltage. The depleted layer thus formed during discharge can isolate charged material that is not close to the current collector, since the discharged material has relatively poor electronic conductivity. Fig. 2 illustrates this condition.

The situation that develops in the nickel electrode that is stored in hydrogen is thus a chemical modification of the active material. This same process is possible in nickel electrodes from nickel cadmium cells, however the incorporation of cadmium hydroxide into the nickel electrode in these cells is likely to offer some protection, since the cadmium should be preferentially reduced during low voltage storage. Likewise, the addition of some

cadmium to the nickel electrode in the nickel hydrogen cell could offer some degree of protection from the degrading effects of a hydrogen precharge.

The net consequence of the degradation illustrated in Fig. 2 is a non-uniform discharge of the nickel electrode, leaving behind an appreciable amount of isolated charged active material. Such a non-uniform discharge can also result from non-uniform loading, sinter that contains large voids, or anomalous phase distributions in the active material. We have developed an empirical test that allows the degree of discharge uniformity to be quantified using a simple procedure. This test is indicated in Fig. 3, where a flooded (31.29% KOH) nickel electrode is discharged at 10 ma/cm^2 following a 32 hr charge at 2 ma/cm^2 (prior to this cycle a standard conditioning cycle is used to stabilize the electrode). A uniformity parameter F is defined as

$$F = Gamma/(Gamma + Beta)$$

where gamma and beta are the relative quantities of the γ-NiOOH and β-NiOOH discharged at the 10 ma/cm^2 rate. It has been empirically found that non-uniform discharge results in isolation of the lower potential gamma phase, as well as a reduced tendency to readily form this phase during the standard recharge employed in this test.

Figure 4 indicates the correlation typically found between active material utilization at the 10 ma/cm^2 discharge rate and the uniformity parameter F. Normal nickel electrodes typically fall between 90 and 110% utilization, with variables such as cobalt level, sinter porosity and uniformity, loading level, and local loading uniformity giving a significant range of utilization across different electrode lots and types. Very uniformly and lightly loaded electrodes with high cobalt levels can easily give utilizations as high as 130% or more, as indicated in Fig. 4. However, nickel electrodes from cells that have experienced fading exhibit a significant reduction in both utilization and the uniformity parameter F. The three points in Fig. 4 having lowest utilization are all from cells that exhibited differing, but significant degrees of capacity fading. Thus, an empirical test such as that indicated in Figs. 3 and 4 can provide a good indication of the origin of degradation in any given nickel electrode. Particularly when the measurements are combined with chemical analyses for $CoHO_2$, the level of which also has been found to correlate with capacity fading (Ref. 2), an excellent diagnostic capability for the root cause of capacity fading emerges.

The capacity fading and redistribution of cobalt that occurs when nickel electrodes are exposed to hydrogen is not neatly recoverable by any obvious method, unless the cobalt depleted layers are quite thin. Empirically, it has been found that repeated high depth-of-discharge cycles or significant long-term overcharge at low rates can recover faded capacity. Since the chemically modified materials remain present in the nickel electrode through such recovery procedures, it is concluded that recovery is successful whenever the layered structures evident in Fig. 2 can be somewhat dissipated. The most obvious approach to such a recovery method is to utilize the physical movement of active material during deep cycles or from oxygen evolution to dissipate such layers through a mixing of the active material layers. Because capacity recovery procedures do not restore the initial phase composition of nickel and cobalt compounds in the active material, a concern exists that the chemical

changes in the nickel electrode will have a deleterious effect on long-term cycle life, i.e. capacity will fade again during cycling much more quickly than otherwise expected.

To evaluate this concern a hydrogen precharged nickel hydrogen cell that had experienced approximately a 30% capacity fade during several years of storage, followed by capacity recovery by means of about 250 80% depth-of-discharge LEO cycles, was placed on an accelerated cycle life test. The results of this life test are indicated in Fig. 5 along with the cycle life behavior of a new cell (no fading) of the same design in the identical life test cycling regime. The conclusion drawn from the test in Fig. 5 is that in spite of the recovery seen in cell capacity, the chemical changes that had taken place in the nickel electrode during storage resulted in loss of about 85% of the cycle life capability of this cell for these test conditions. In view of these results, it clearly is very desirable to avoid the chemical changes responsible for capacity fading.

Capacity Fading Mechanisms in Nickel Precharged Cells

A nickel precharged nickel hydrogen cell is built with more capacity in the nickel electrode than there is hydrogen gas available for the negative electrode. Thus in the fully discharged state typically utilized for cell storage, the cell contains no hydrogen gas, but does contain some remaining charge in the nickel electrode active material. Because the charged nickel electrode active material is generally unstable relative to oxygen, it will evolve some level of oxygen gas in the stored cell. Thus, this cell will contain an oxidizing atmosphere of gas during storage, which will make the platinum catalyst electrode become an oxygen electrode. The relative electrode capacities typically desired in this cell design are indicated in Fig. 6. So that the usable capacity of the cell is not reduced by the nickel precharge, the cell is normally built so that the hydrogen is fully consumed only by discharge after the active capacity of the nickel electrode is depleted, i.e. during discharge of the residual capacity. With typical nickel electrodes this approach places an upper limit of about 10-20% nickel precharge on the cell, with a concomitant decrease in the operating pressure of the cell. Although higher precharge levels may be used, they can reduce the capacity of the cell below that which could otherwise be attained.

The positioning of the relative nickel and hydrogen electrode capacities indicated in Fig. 6 has some potential problems. First, if the nickel electrode has an extremely high utilization, the band of residual charge will be quite narrow, resulting in a very narrow window of acceptable precharge. In this situation it is probably more desirable to increase the nickel precharge into the active capacity region, instead of risking cell degradation if the nickel precharge is insufficient. It should be noted here that any oxidation of sinter or other materials in the cell during operation will tend to increase the amount of hydrogen in the cell. Thus, some excess nickel precharge is highly desirable to get the cell through early life cycling and storage without developing a hydrogen precharge.

The second point to note in Fig. 6 is that any significant shifts in the amounts of either residual capacity or unavailable capacity during cell operation can convert a nickel precharged cell into a cell that is effectively hydrogen precharged. There are several

operational conditions commonly encountered during cell testing that can shift the amounts of residual and unavailable capacity significantly, and thus are to be avoided just prior to storage periods except under carefully controlled test conditions. The first of these conditions is indicated in Fig. 7, and involves allowing the charged cell to stand open circuit prior to discharge. Such open circuit stand, which is commonly used for charge retention tests, causes most of the residual capacity to become unavailable through charge redistribution processes described in Ref. 3. This can easily convert a nickel precharged cell into a cell that contains undischargeable hydrogen, although this hydrogen may eventually be depleted by self-discharge processes. Storage of this cell at a low voltage, however, will clearly initiate the processes responsible for capacity fading in the hydrogen precharged nickel hydrogen cell. Thus, a common test to which nickel hydrogen cells are exposed is capable of temporarily generating conditions known to degrade cell performance.

Another relatively common test condition that can have a similar effect is indicated in Fig. 8. Here the cell is simply discharged at low temperature, which significantly increases the amounts of both residual and unavailable capacities. This is primarily due to the reduced conductivity of the active material at lower temperatures. Here again, the unavailable capacity in the discharged cell can rise to exceed the level of hydrogen in the cell, thus leaving a temporary hydrogen precharge condition. The scenarios presented in Figs. 7 and 8 clearly show that a nickel precharged cell should be carefully prepared for a storage period, employing a standard preparation cycle which is guaranteed to leave the desired state of precharge.

A number of other conditions in the nickel hydrogen cell have been found to cause increases in the residual and unavailable capacities in the nickel electrodes. One of these conditions occurs when silicate contaminants build up to levels much above 1000 ppm in the KOH electrolyte, particularly when the cell is operated at low temperatures. The typical sources for silicate contaminants are dirt or dust particles, or the presence of silicate based minerals such as asbestos in the separator. These silicate containing materials generally lose silicate by replacement with hydroxide from the electrolyte over time, thus allowing silicate levels to build up in the electrolyte during extended storage. The rate of this buildup can vary significantly, as the rate at which different silicate minerals are attacked by KOH varies tremendously. For very slow processes of this kind, low temperature storage is clearly beneficial. However, the best solution to this problem is simply to insure, through attention to cleanliness and appropriate design, that negligible amounts of silicate minerals are present in the cell.

The mechanism by which silicate affects the nickel electrode is not fully understood (Ref. 4). Empirical evidence indicates that silicates are incorporated into the nickel electrode active material during overcharge, as evidenced by anomalous increases in overcharge voltage. Whether this results from silicate crystallization, dehydration of the active material by the silicate, or some other mechanism is not fully certain. This incorporation is accompanied by a significant increase in the resistance of the nickel electrode. The added resistance component has a large temperature coefficient, thus affecting cell charge and discharge voltage markedly at low temperatures. Typically, as the cell is discharged the silicate will come out of the nickel electrode and the resistance will drop. The result can

be a significantly depressed discharge plateau voltage as indicated in Fig. 9, which in extreme cases can exhibit a pronounced minimum part way through the discharge. The results of Fig. 9 are for small laboratory cells operated at 600 psia of hydrogen, and with calcium silicate added to the interface between the nickel electrode and the zircar separator. The behavior of Fig. 9 developed gradually over approximately 40 100% depth-of-discharge cycles at 25 deg C, performed over a period of 44 days.

Clearly, silicate contaminants can decrease cycle life, although the extreme case represented in Fig. 9 may not be representative of the silicate levels from spot contamination. However, cells containing silicate based separators such as asbestos have exhibited anomalous discharge voltage profiles much like those of Fig. 9, ranging in severity from causing failure within the first 100 cycles, to causing failure after 12,000 LEO cycles at 40% depth-of-discharge.

Another contaminating material that has been found to change the relative amounts of residual and unavailable capacity is sulfate ions in the electrolyte (Ref. 4). More than 300-500 ppm of sulfate in the electrolyte can result in significant increases in the amount of capacity discharged on the second plateau, particularly when combined with low temperature operation and charged open circuit stand. This behavior is indicated in Fig. 10, again for small nickel hydrogen cells operated at about 600 psia with calcium sulfate added between the zircar separator and the nickel electrode. In actual nickel hydrogen cells, the sources for such sulfate materials have been found to be spot contamination by mineral particles (gypsum, $CaSO_4$, most commonly), and separators. Sulfates have been found in both zircar and asbestos separator materials.

One effect that sulfate ions can have on the nickel electrode is also a real concern for a number of other anionic contaminants, i.e. accelerated corrosion of the sinter structure. Clearly this process is capable of converting a nickel precharged cell into a hydrogen precharged one either during storage or during early cycling prior to storage. In a flooded life test consisting of 6500-7000 100% depth-of-discharge cycles, the rate of corrosion in the presence of sulfate ions was found to be 2 to 5 times greater than that in the absence of sulfate.

The mechanism by which sulfate ions alter the performance of the nickel electrode is again not fully understood. It seems most likely that the sulfate ions react with cobalt sites in the active material, decreasing active capacity by forming traps for the normally mobile protons in the active material. The complex that sulfate forms with cobalt appears to be somewhat soluble in KOH. After 6500 cycles in sulfate containing electrolyte a nickel electrode was observed to have lost about 50% of its total cobalt additive, with the lost cobalt being deposited onto the counterelectrode in the flooded cell.

Figure 11 indicates capacity performance over 6500-7000 accelerated cycles for flooded nickel electrodes in 31% KOH with 0.5 g/100 cc of calcium sulfate added. This test was to 100% depth-of-discharge, with 100% depth defined as 0.0 volts vs. Hg/HgO at 100 ma/cm². Charge return was 100% of the beginning of life capacity of each electrode as measured at the 10 ma/cm² discharge rate. After 6500 cycles, the electrode cycled with added sulfate

exhibited a discharge voltage plateau depressed to near the 0.0 volt level, thus its capacity appeared to suddenly drop. Actually the discharge voltage of this electrode had degraded continuously during the cycling after about cycle 1000. The electrode cycled with no sulfate had experienced only about a 20 mv drop in the discharge plateau after nearly 7000 cycles, and essentially no capacity loss. After almost 7000 cycles this test was stopped based on the observation that the electrode cycled with sulfate had failed while the electrode cycled with no sulfate remained far from failure.

In Fig. 11 the electrode cycled with no sulfate exhibited a normal capacity profile over cycle life. A capacity rise during the initial 2000-3000 cycles was followed by a level then a gradually dropping capacity. With sulfate present, however, a very different behavior was seen. The initial rapid drop, then rise in capacity over the first 800 cycles appears to be associated with the slow incorporation of sulfate species into the cobalt sites within the active material. Thereafter, while capacity appears to be relatively stable, the cobalt in the active material is slowly undergoing solubilization causing the active material to lose cobalt, as well as experiencing accelerated corrosion. About 10% of the sinter had corroded after 6500 cycles. It is likely that the combination of these changes played a significant role in the earlier failure of the electrode exposed to sulfate.

A final chemical reaction of potential concern during the storage of a nickel precharged cell involves the platinum electrode. As was previously discussed, in a discharged nickel precharged cell the platinum catalyst electrode adopts the potential of an oxygen electrode, which is near that of the nickel electrode, depending on the pressure of oxygen in the cell. At this potential the platinum catalyst will undergo oxidation, forming a layer of $Pt(OH)_2$ on its surface. In KOH electrolyte this compound has some solubility, thus the platinum does not fully passivate. The result is an equilibrium level of $Pt(OH)_4^=$ in the electrolyte after an extended storage period. These platinate ions can migrate to the nickel electrode, where they can participate in various chemical reactions.

Platinate ions appear to catalytically interact with the precharge in the nickel electrode. These ions appear to slowly associate with adjacent cobalt and nickel sites to form a CoNiPt oxyhydroxide complex. The platinum in this complex is in equilibrium with platinate ions in the electrolyte. Cell recharge will plate the platinum from the platinate species back onto the catalyst electrode, thus causing the platinum to leave the complex formed in the nickel electrode by the resulting shift in the equilibrium. However, this process leaves behind in the nickel electrode a relatively stable NiCo oxyhydroxide compound. This reaction is capable of consuming much of the precharge in the nickel electrode. This reaction provides a rationale for using a level of precharge significantly greater than the amount of cobalt in the nickel electrode.

The NiCo oxyhydroxide compound formed in a nickel precharged cell provides an unambiguous signature indicating whether the precharge has indeed remained intact over the life of the cell. Figure 12 shows the voltage signature for this compound. While not having a high electrochemical activity, in a slow scan voltammetric measurement (Fig. 12 uses less than a 2 μV/sec sweep rate) reduction of a well defined phase is seen at about 0.15 volts vs. Hg/HgO. This is a potential region where a normal nickel electrode has a

clean minimum in its electrochemically active constituents. Complete reduction of this compound causes it to dissociate within a 24 hr period. Subsequent oxidation of the nickel electrode shows no trace of being able to regenerate this structure, unless done very quickly, whereupon very limited reversibility is seen. Thus, the observation of the 0.15 volt peak of Fig. 12 in a nickel electrode from a stored cell is good evidence that the cell has not experienced temporary conversion to a hydrogen precharged condition at any time in its past history. Conversely, the complete absence of this structure in nickel electrodes from a stored cell with nickel precharge suggests that at some time the precharge has been compromised. We have in fact used this method in several instances to detect conditions that can temporarily compromise the nickel precharge in a cell.

The long term effects of forming NiCo oxyhydroxides in nickel electrodes is uncertain. After extensive cell cycling there will clearly be sufficient hydrogen generated (from corrosion) to reduce these materials if a cell is fully discharged, such as would happen during reconditioning. The products of this reduction process are not presently known. It is clearly possible that these products could initiate cobalt segregation processes. In view of these uncertainties, and considering the long-term storage and test times required to address these issues, it seems best to avoid the formation of these NiCo oxyhydroxide compounds by not allowing the platinum electrode to rise to the oxygen potential.

Summary of Processes Affecting Stored Cells

Figure 13 attempts to summarize the principal processes that can occur in stored nickel hydrogen cells. At the bottom of Fig. 13, the situation in a hydrogen precharged cell is shaded in. The depleted nickel electrode is reduced to a potential near that of the hydrogen electrode, giving an open circuit cell potential near zero. At these potentials the nickel and cobalt hydroxides in the active material can undergo reduction, and if the potential is subsequently increased, the dicobaltite ion can form from cobalt hydroxide. Above about 0.3 volts vs. hydrogen the nickel sinter begins to oxidize and develops a passivation layer, becoming fully passivated above about 0.5 volts.

The shaded region at the top of Fig. 13 indicates the reactions that can take place during storage of a nickel precharged cell. The platinum electrode is driven above the potential at which it can oxidize to the potential dictated by the oxygen in the cell, again giving a cell voltage of 0 to +0.3, depending on the exact oxygen pressure in the cell. Formation of platinate ions and their reaction with the nickel electrode can eventually reduce the potential of the nickel electrode, thus driving the open circuit cell potential negative. When the CoOOH couple is also included, it is possible to have the open circuit potential of the stored cell go negative by up to -0.3 volts. Thus the open circuit potential of a stored nickel precharged cell can drift between about 0.3 and -0.3 volts, depending on the oxygen pressure and the chemical state of the nickel precharge.

The most interesting aspect of Fig. 13 is that there is a region in the middle where none of the reactions considered here are possible except nickel corrosion. However, at cell potentials above 0.5 volts and below 1.0 volt, nickel metal is passivated, and actually more

stable than in ambient atmosphere, assuming that no anionic species are present that can accelerate corrosion by breaking down the passivation layer. Whether a cell has a hydrogen precharge or a nickel precharge, it can be maintained in this window of stability simply by maintaining a cell potential of 0.5 to 1.0 volts. This appears to be an ideal storage condition for a nickel hydrogen cell, one which eliminates concern over the precise details of precharge, its level, and its stability.

Summary of Causes for Capacity Fading

In general, capacity fading has been found to result from having hydrogen in contact with the nickel electrode when its potential is below 0.5 volts. Clearly, hydrogen precharged cells meet this condition. It is also possible however, to generate a temporary hydrogen precharged condition by the cycling environment and the cycling method for the cell. Finally, chemical modification of the nickel electrode by reaction with platinum, silicates, sulfates, or perhaps other species as well, can impact the availability of nickel precharge to protect the stored cell from fading.

Recommendations to Avoid Fading

1. Use nickel precharge. It avoids reducing potentials at the nickel electrode, which have been shown to be capable of rapidly degrading cell capacity. It also reduces operating pressure.

2. Maintain a controlled potential of 0.5 to 1.0 volts on each cell during storage periods. This prevents platinum oxidation in nickel precharged cells, and prevents degradation from hydrogen precharge, should it ever develop in the life of a cell.

3. Store cold (about 32 deg F). This will slow all degradation processes, including those that we have not yet seen.

4. Always go into storage using a well defined procedure designed to maximize the availability of active precharge in the nickel electrode. A recommended procedure is to simply precede storage with one 20 deg C capacity cycle:
   - Charge fully at 20 deg C, with no open circuit stand time allowed.
   - Discharge at C/2 to 0.7 volts for each cell.
   - Resistive letdown to 10 mv, or for 16 hr maximum.

Storage at voltages above 1 volt or on trickle charge or top-charge will also keep the degradation processes discussed above in abeyance. However, concern exists regarding sinter corrosion at these more oxidizing potentials. It is this concern that suggests the recommended 1.0 volt upper limit for a storage potential.

References

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Normal Hydrogen Precharged
Nickel Hydrogen Cell
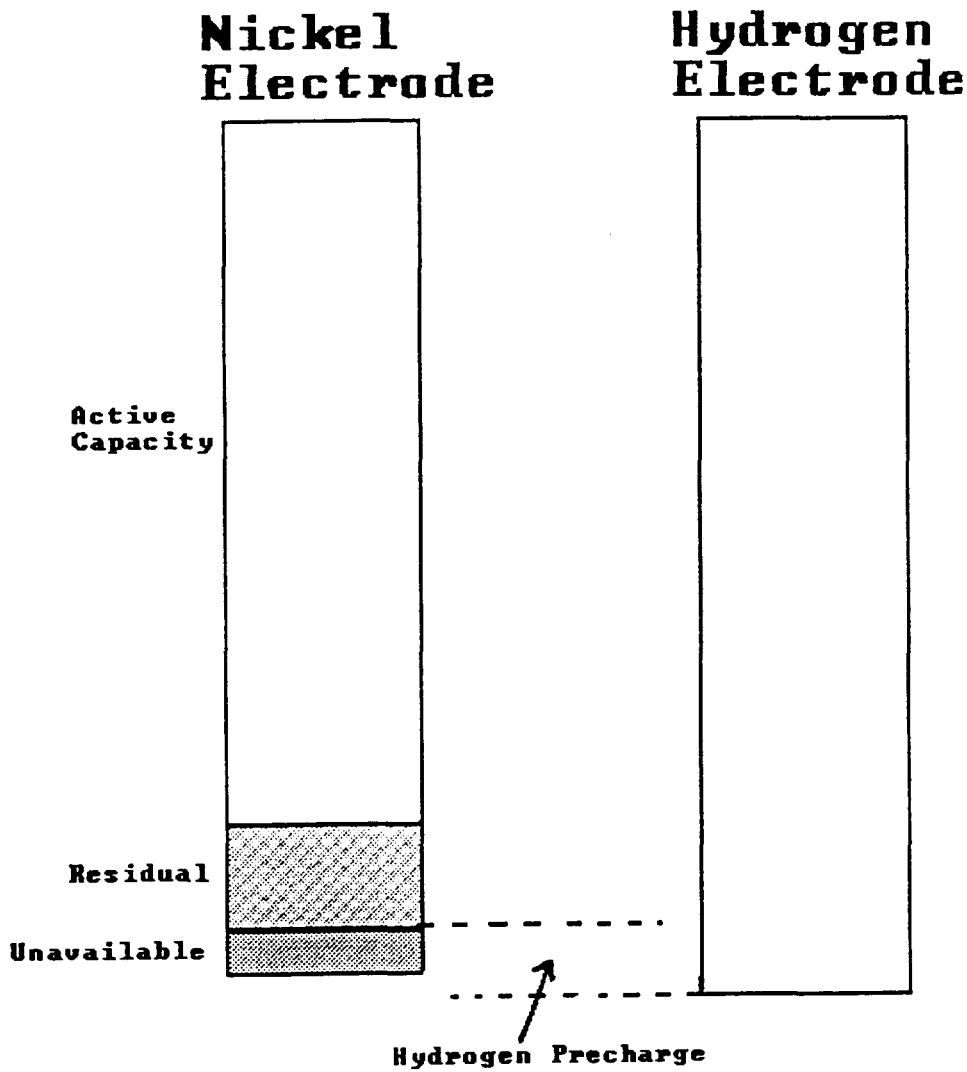
FIGURE 1.

FIGURE 2.

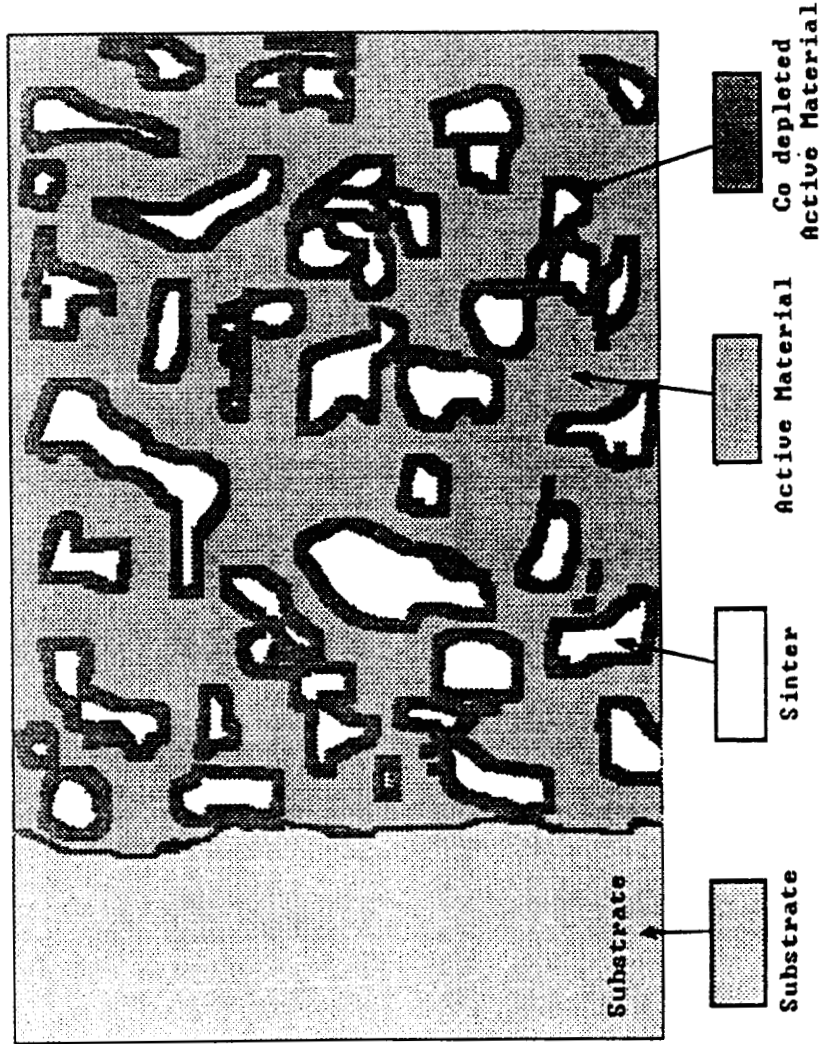Movement of Cobalt
in Active Material
of Nickel Electrode

FIGURE 3.
Definition of Uniformity Parameter, F
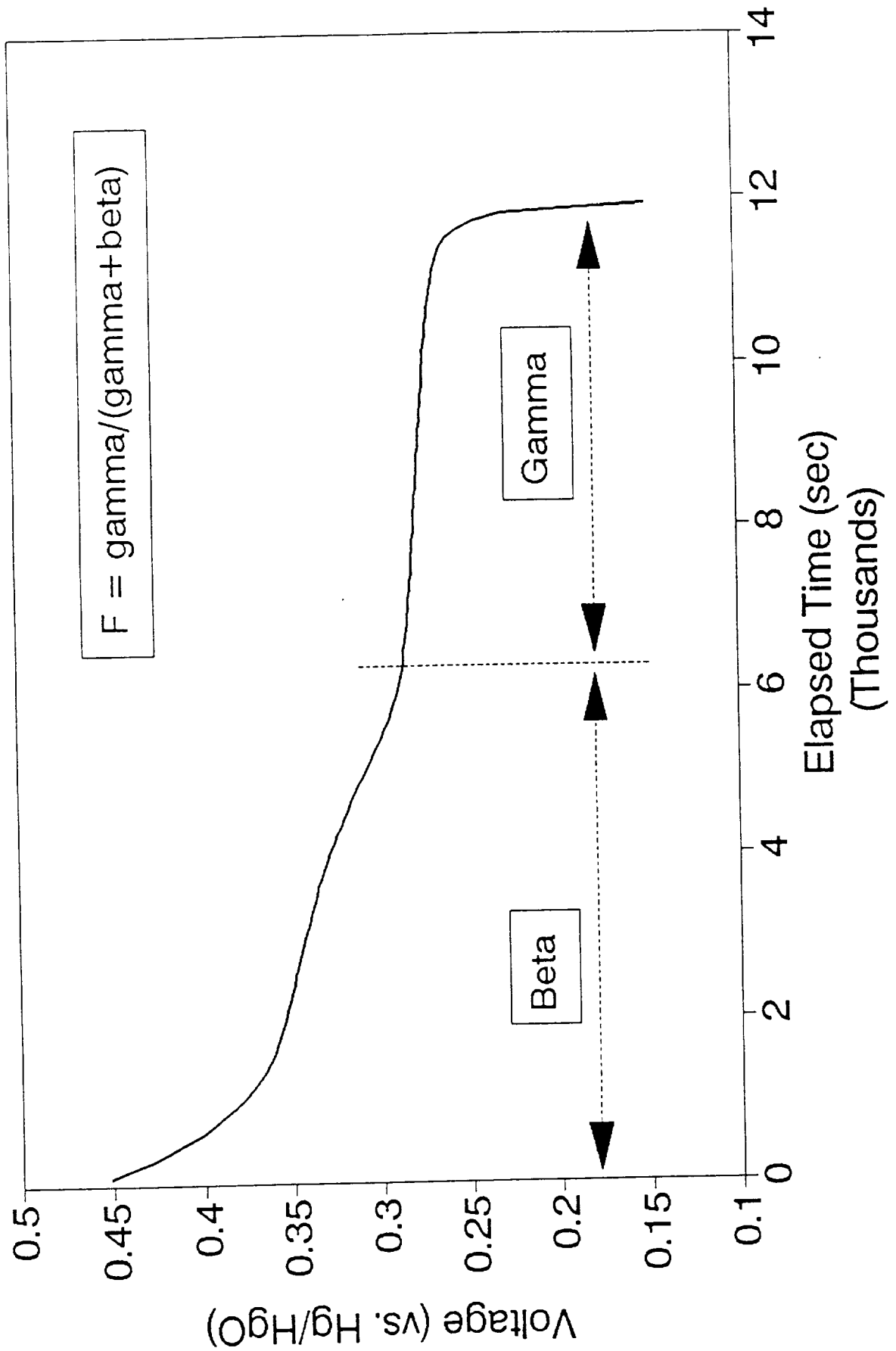31% KOH, 10 ma/cm2 disch after 32 hr ch

F = gamma/(gamma+beta)

Gamma

Beta

Elapsed Time (sec)
(Thousands)

Voltage (vs. Hg/HgO)

FIGURE 4.

Nickel Electrodes in 31% KOH
Utilization vs. Uniformity Parameter
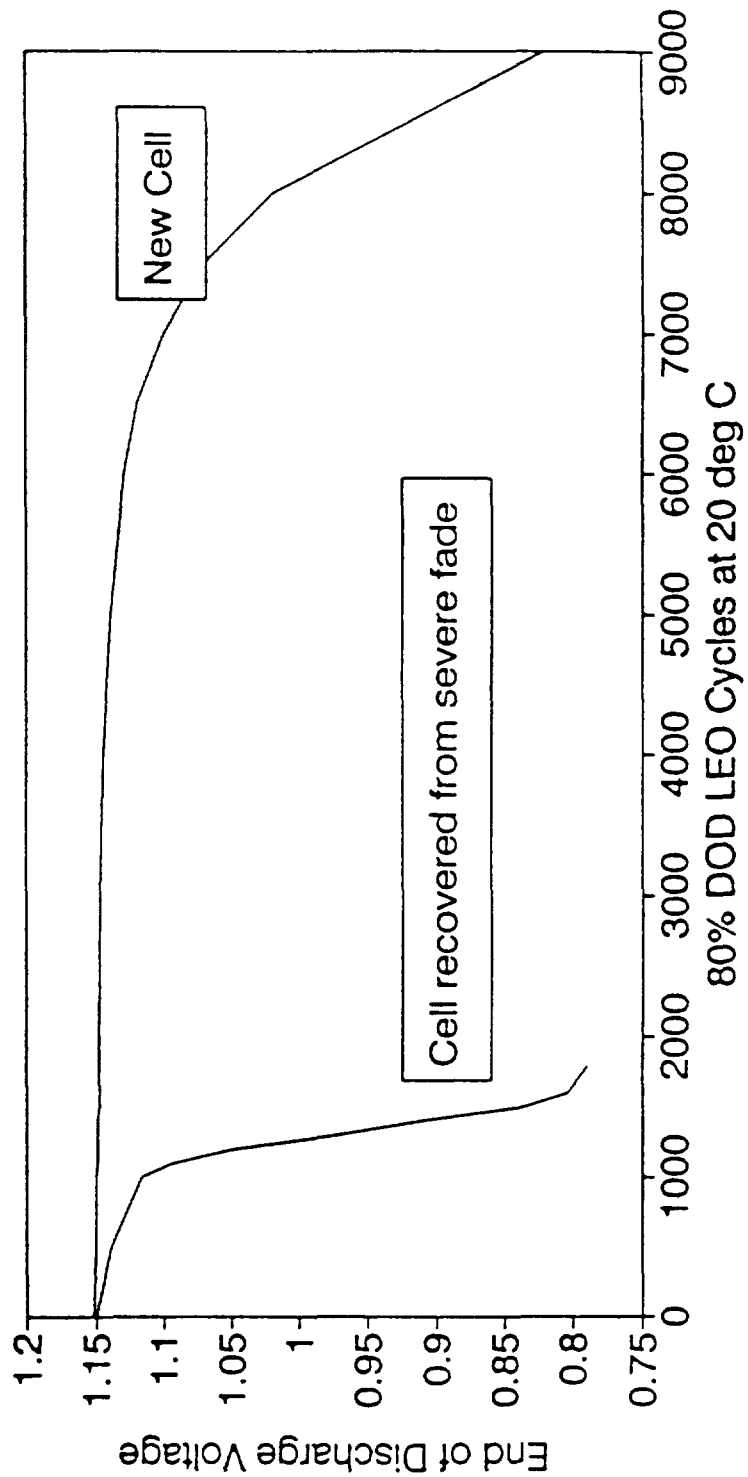
Utilization (%of theoretical)

Uniformity Parameter
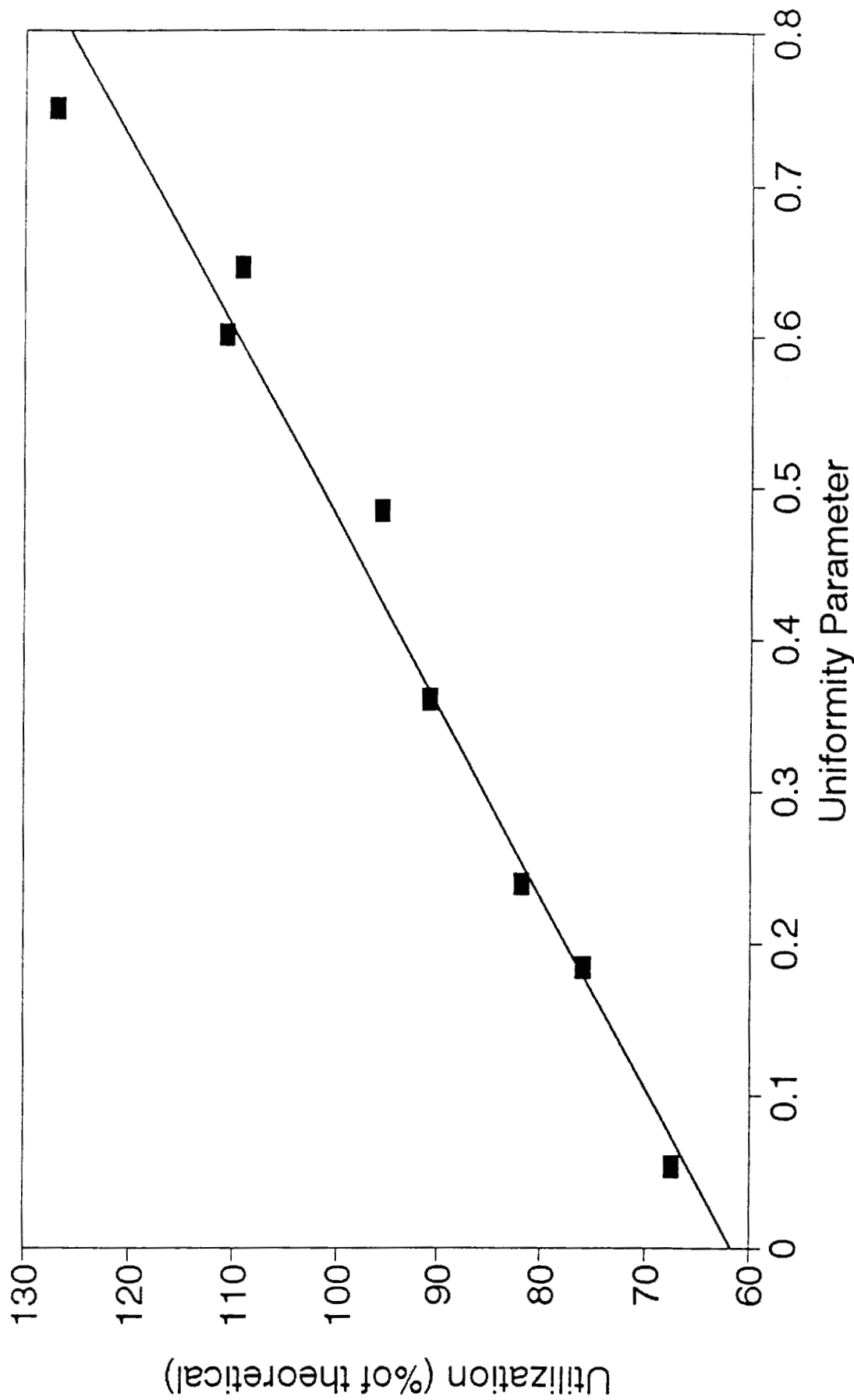
FiGuRE 5.

PERFORMANCE OF FADED CELL AFTER CAPACITY RECOVERY
BY EXTENSIVE CYCLING

- RAN LIFE TEST: 80% DOD, LEO CYCLE, 20.DEG C, 1.05 RETURN RATIO

- CONCLUSION: FADING DEGRADES CYCLE LIFE SIGNIFICANTLY, EVEN
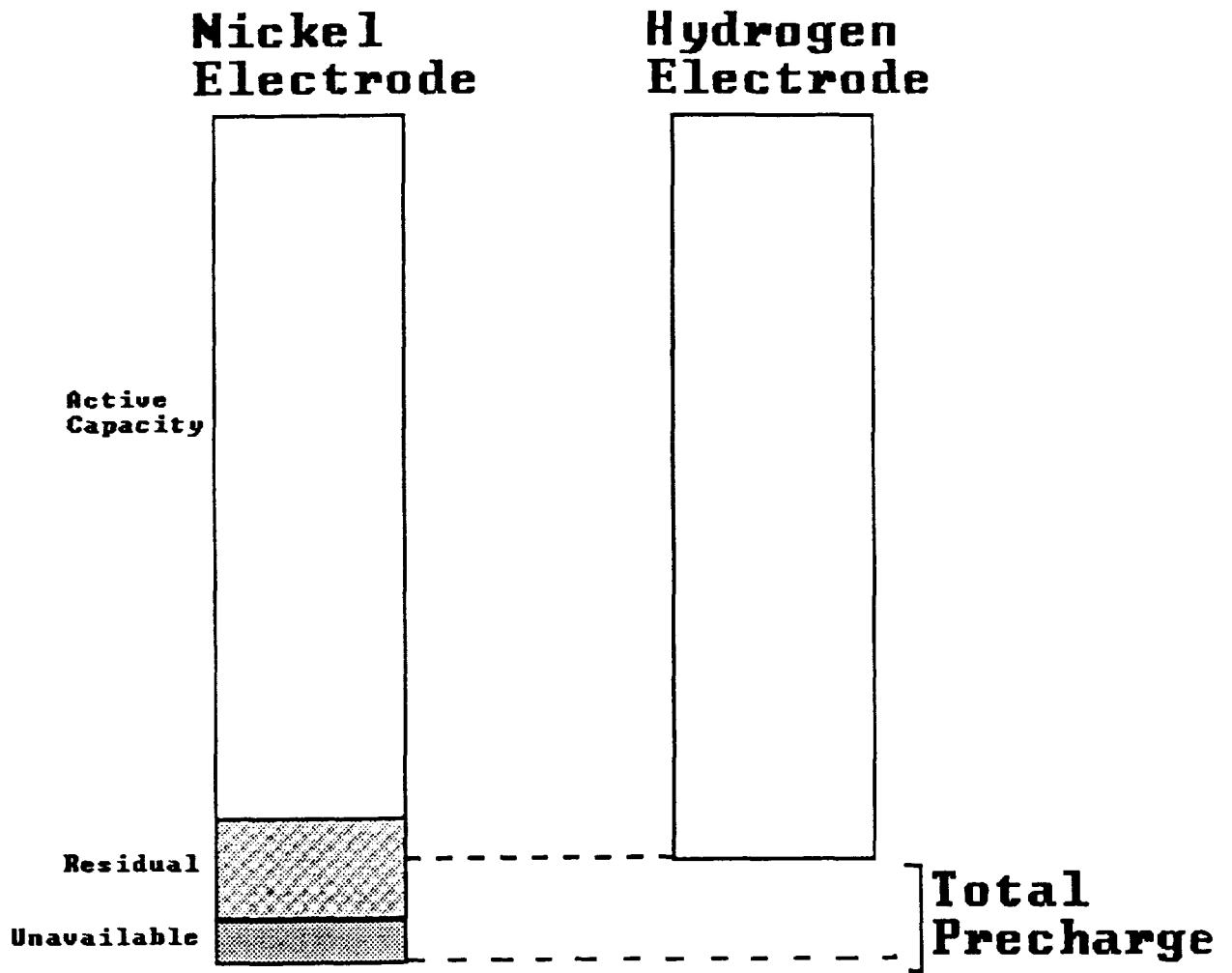 WITH APPARENT CAPACITY RECOVERY

Normal Nickel Precharged Cell

Nickel Electrode

Hydrogen Electrode

Active Capacity

Residual

Unavailable

Total Precharge

FIGURE 6.

Nickel Precharged Cell After Stand in Partly Charged or Open-Circuit Charged State
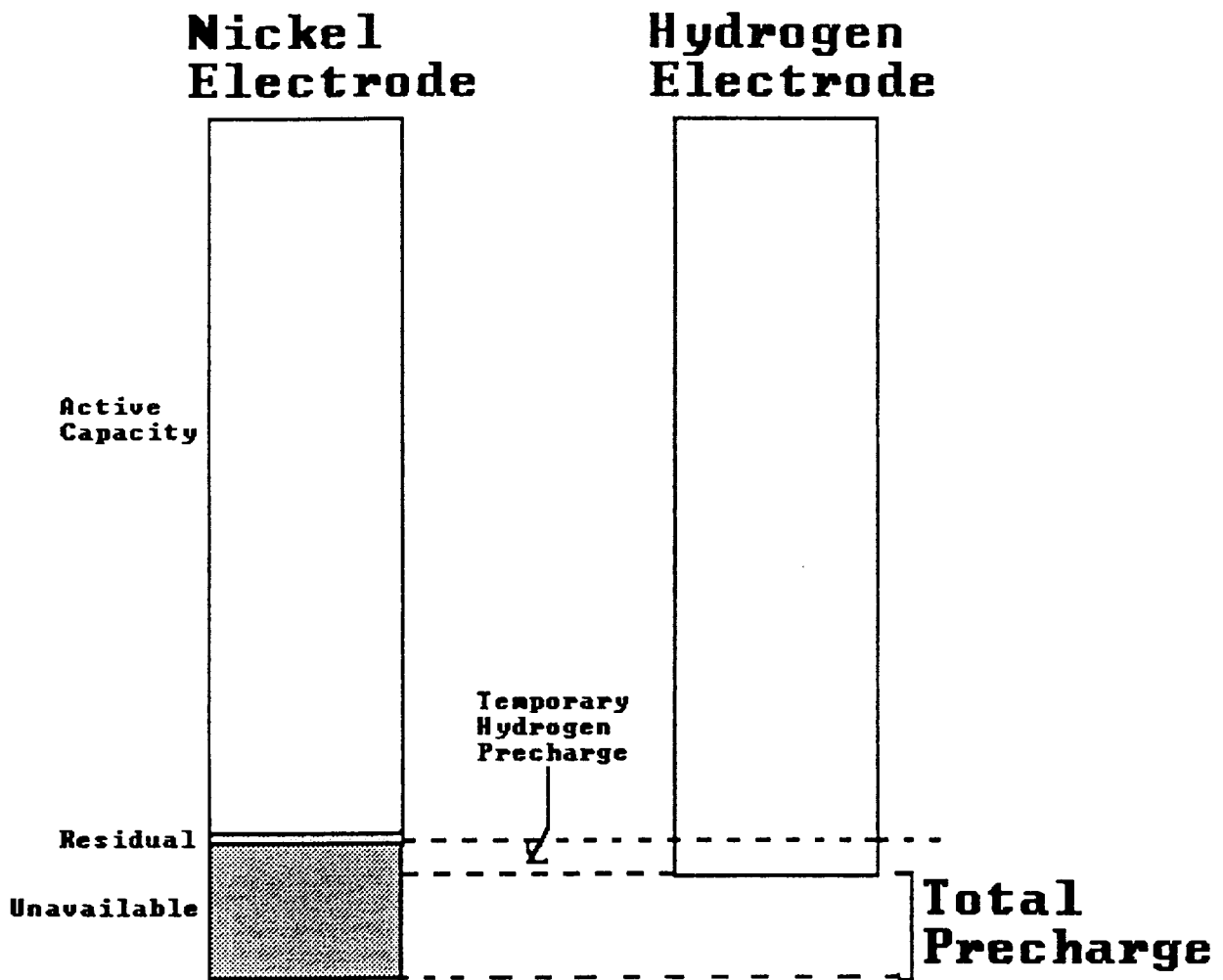
FIGURE 7.

Nickel Hydrogen Cell After
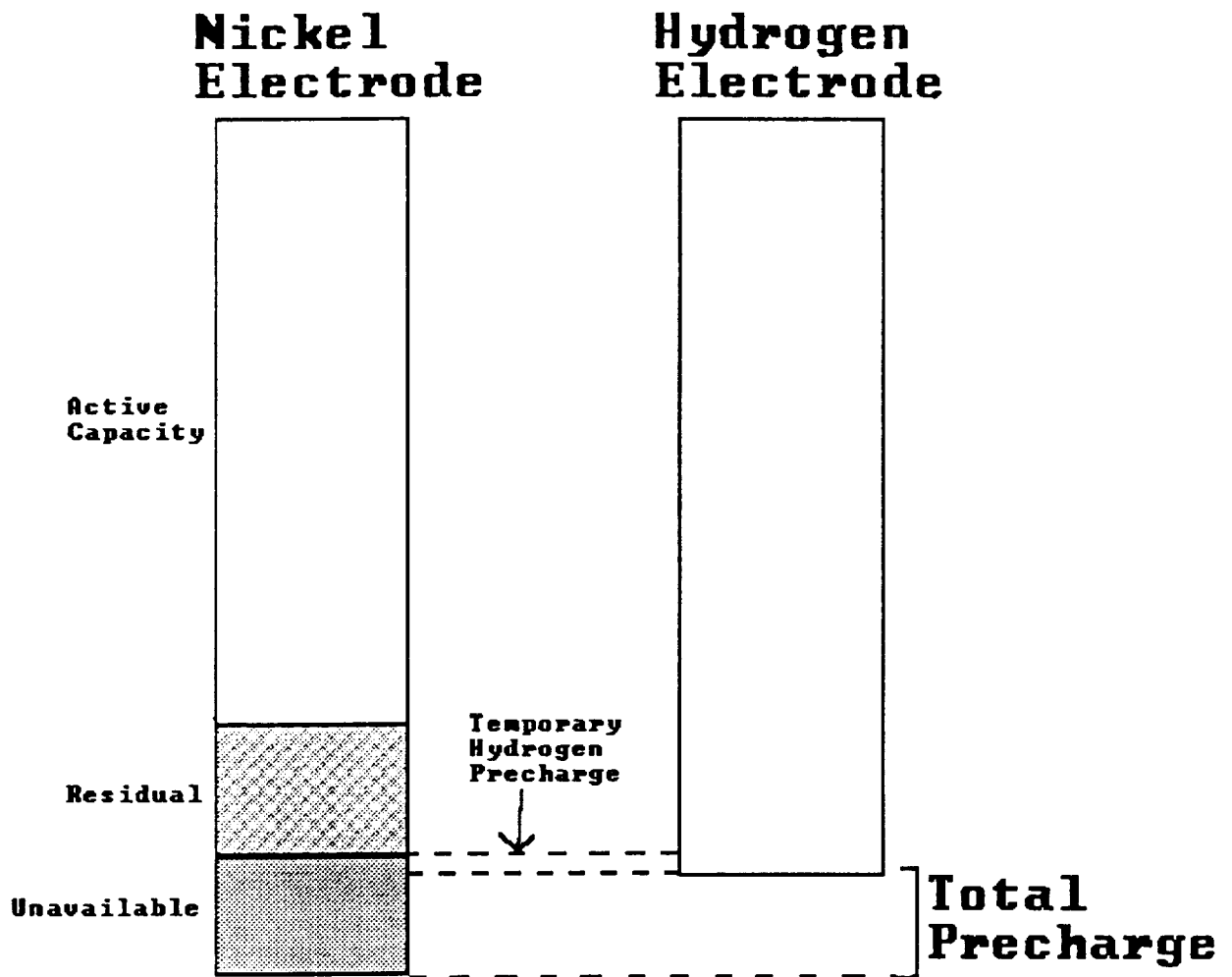# a Low-Temperature Discharge

Nickel
Electrode

Hydrogen
Electrode

Active
Capacity

Temporary
Hydrogen
Precharge

Residual

Unavailable

]Total
]Precharge

FIGURE 8.

Discharge of NiH2 Cell with Silicates

FIGURE 9.

15 ma/cm2, 0 deg C

Legend:
- No silicate
- 4 mg silicate
- 10 mg silicate

Y-axis: Voltage
X-axis: Discharge Time (sec)
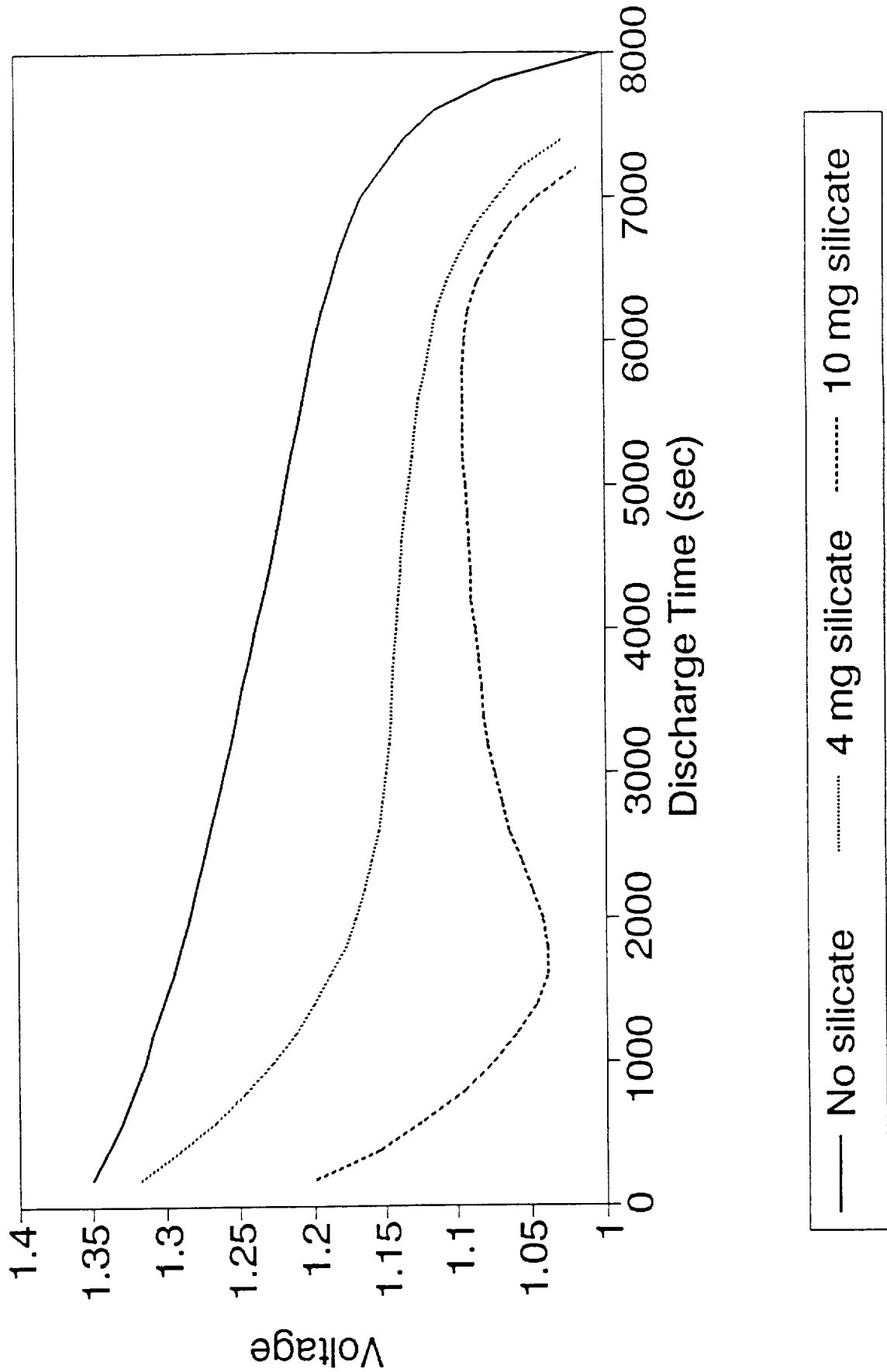
Discharge of NiH2 Cell with Sulfate
15 ma/cm2, 20 deg C

FIGURE 10.

Legend:
— No sulfate
----- 6.4 mg sulfate
······ 10.6 mg sulfate

x-axis: Fraction of Capacity Discharged
y-axis: Cell Voltage
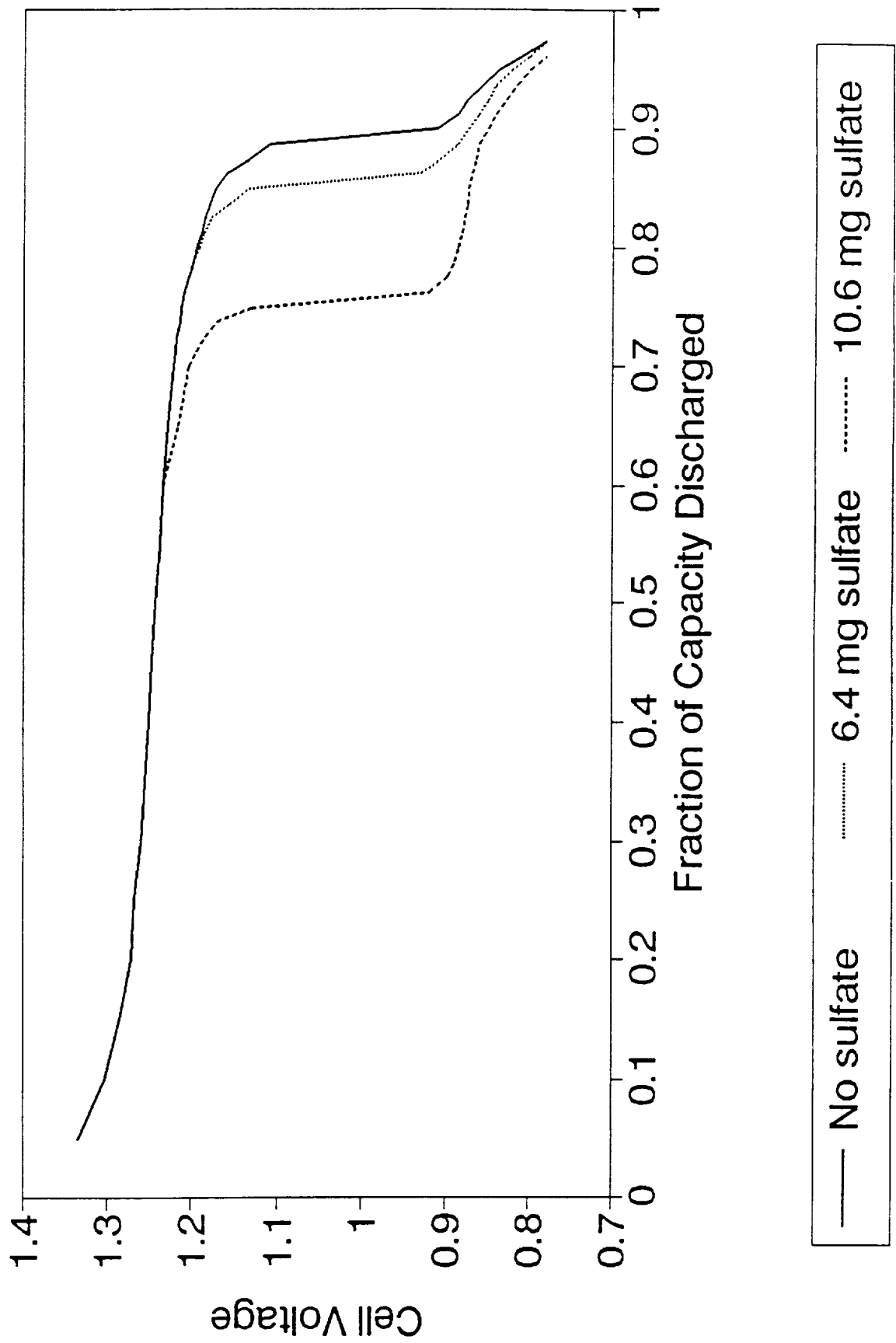
FIGURE 11.

Cycling of Ni Electrode with Sulfate
100 ma/cm2, 23 deg C

Capacity (mAh/cm2)

100% DOD cycles

—— No Sulfate .... With Sulfate
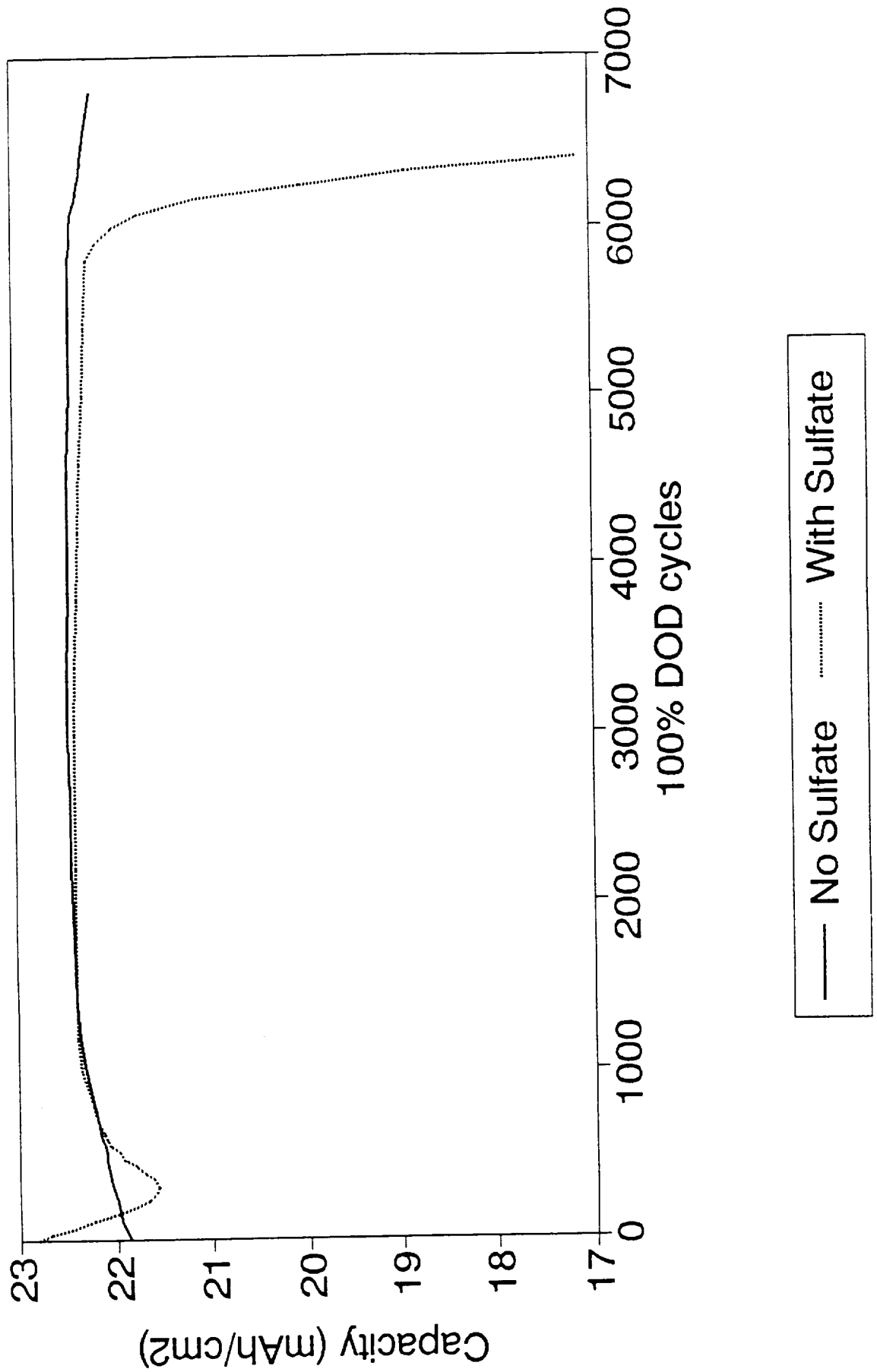
FIGURE 12.

Reduction State Density vs. Potential
Nickel Electrodes from Stored Cells

Legend: —— Nickel Precharge   ·········· Hydrogen Precharge

X-axis: Voltage vs. Hg/HgO

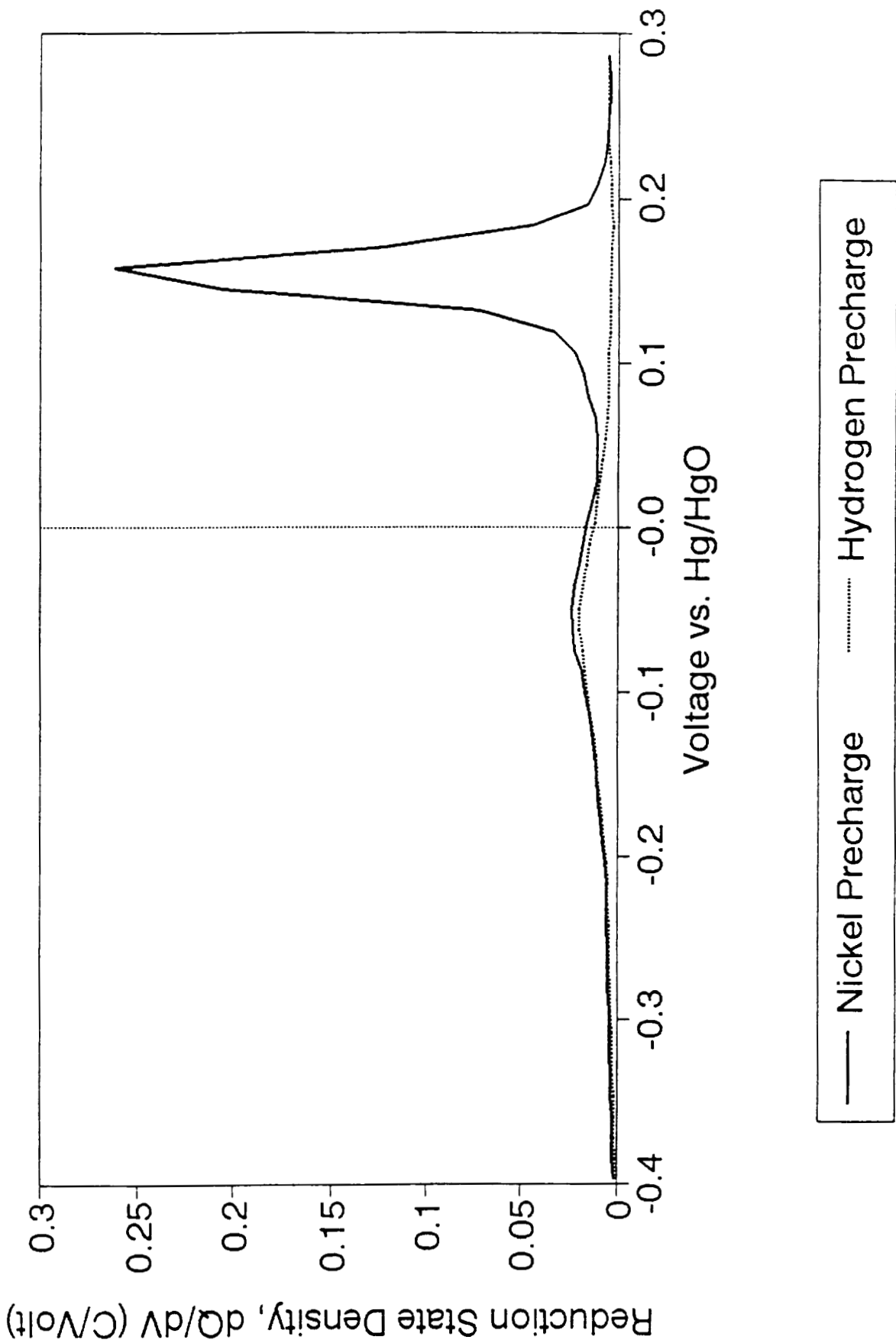Y-axis: Reduction State Density, dQ/dV (C/Volt)

FiGuRE 13.

Nickel Hydrogen Cell
Reactions and Regions
of Stability

Oxygen

Platinum

NiOOH

NiCoPtOOH

CoOOH

$Pt(OH)_6^=$

Nickel Precharge

-.3 to +.3 volts

Ni oxidation (+/-)
Pt oxidation
NiOOH oxygen evol
NiCoPtOOH formation

Stable Potential
Region
0.4 to 1.0 volts

Ni oxidation

H_2 Precharge

About 0 V Open
Circuit Potential

$Ni(OH)_2$ $Co(OH)_2$
Reduction

Hydrogen

Ni Passivation

$Ni(OH)_2$ $Co(OH)_2$

$HCoO_2^-$

Nickel Electrode

Hydrogen Electrode