

Short communication

## Cause of the memory effect in “nickel” electrodes

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Available online 15 November 2006

### Abstract

Several types of commercial batteries employ the  $\text{H}_2\text{NiO}_2\text{--HNiO}_2$  (or  $\text{Ni(OH)}_2\text{--NiOOH}$ ) reaction in their positive electrodes. Such batteries often exhibit a so-called “memory effect” in which the available capacity at useful voltages noticeably decreases if they are used under conditions in which they are repeatedly only partially discharged before being recharged. However, if such cells are deeply discharged, the apparently lost capacity can be recovered. It is shown that these phenomena can be rationally explained by considering the reactions in the “nickel electrode” in terms of the thermodynamics of the ternary H–Ni–O system.

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*Keywords:* Nickel electrode; Memory effect; Second discharge plateau;  $\text{HNi}_2\text{O}_3$

### 1. Introduction

It is often found that batteries with “nickel” positive electrodes, e.g. Cd/Ni, hydride/Ni, Zn/Ni, Fe/Ni, and  $\text{H}_2/\text{Ni}$  cells, have a so-called “memory effect”, in which the available capacity apparently decreases if they are used under conditions in which they are repeatedly only partially discharged before recharging. In many cases these batteries are kept connected to their chargers for long periods of time. It is also widely known that this problem can be “cured” by subjecting them to a slow, deep discharge.

The phenomena that take place in such electrodes have been studied by many investigators over many years, but no rational and consistent explanation of the “memory effect” related to “nickel” electrodes has emerged. Although it has important implications for the practical use of such cells, some of the major reviews in this area do not even mention this problem, and others give it little attention and/or no explanation.

A different “memory effect” is often found upon overcharge of Cd/Ni cells that is related to the cadmium negative electrode, but this will not be discussed here.

In studying this apparent loss of capacity, a number of investigators have shown that a second plateau appears at a lower potential during discharge of “nickel” electrodes [1–16]. Importantly, it is found that under low current conditions the total length of the two plateaus remains constant. As the capacity on

the lower one, sometimes called “residual capacity”, becomes greater, the capacity of the higher one shrinks. The relative lengths of the two plateaus vary with the conditions of prior charging. This is shown schematically in Fig. 1.

Since the capacity of the lower plateau is at about 0.78 V versus the hydrogen electrode, it is generally not useful for most of the applications for which nickel electrode batteries are employed. The user does not see this capacity, but instead, sees only the dwindling capacity on the upper plateau upon discharge. Thus it is quite obvious that the appearance of this lower plateau is an important component of the memory effect.

It is also found that this lower plateau and the memory effect both disappear if the cell is deeply discharged. Thus the existence of the lower plateau, and its disappearance, are both obviously related to the “curing” of the memory effect.

Although considerable effort has been expended to explain the structural and mechanistic basis for this behavior, it is fair to say that no consensus has been reached.

The purpose of this paper is to show how these phenomena can be explained on the basis of available thermodynamic and structural information by using the ternary Gibbs triangle for the H–Ni–O system as a thinking tool.

### 2. Mechanistic features of the operation of the “nickel” electrode

The microscopic mechanism of the basic operation of these electrodes has been discussed in a number of places [17–21]. It involves an insertion reaction that results in the translation

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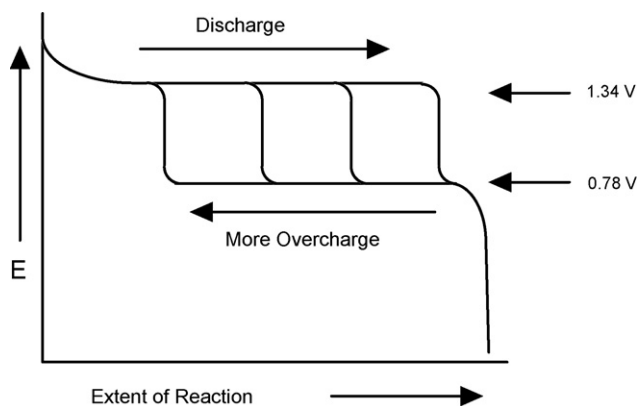


Fig. 1. Schematic representation of the two discharge plateaus. With increasing overcharge the length of the upper one decreases and the lower one increases.

of a two-phase interface between  $\text{H}_2\text{NiO}_2$  and  $\text{HNiO}_2$ , both of which are vario-stoichiometric (have ranges of stoichiometry). The  $\text{H}_2\text{NiO}_2$  is in contact with the alkaline electrolyte, and the  $\text{HNiO}_2$  is in contact with the metallic current collector [22]. The outer layer of the  $\text{H}_2\text{NiO}_2$  phase is pale green and is predominantly an ionic conductor, allowing the transport of protons to and from the two-phase  $\text{H}_2\text{NiO}_2/\text{HNiO}_2$  boundary.  $\text{HNiO}_2$  is a good electronic conductor, and is black. The electrochemical reaction takes place at that ionic/electronic two-phase interface. This boundary is displaced as the reaction proceeds, and the motion of the color boundary has been experimentally observed [23]. When the electrode is fully reduced, its structure consists of only  $\text{H}_2\text{NiO}_2$ , whereas oxidation causes the interface to translate in the opposite direction until only  $\text{HNiO}_2$  is present. Although these are both ternary phases, the only compositional change involves the amount of hydrogen present, and the structure of the host “ $\text{NiO}_2$ ” does not change. Thus this is a pseudo-binary reaction, although this is a ternary system, and the potential is independent of the overall composition; i.e. the state of charge. The thermodynamic basis for this will be discussed later.

After the  $\text{H}_2\text{NiO}_2$  has been completely consumed, and the  $\text{HNiO}_2$  phase comes into contact with the aqueous electrolyte it is possible to obtain further oxidation. This involves a change in the hydrogen content of the “ $\text{HNiO}_2$ ” phase. The variation of the composition of this single phase results in an increase in the potential from this two-phase plateau to higher values, as is expected from the Gibbs phase rule.

After the low-hydrogen limit of the composition of the “ $\text{HNiO}_2$ ” phase is reached, further oxidation can still take place. This is shown by the fact that another potential plateau is observed, and oxygen evolution occurs. This is often called “overcharging”, and obviously involves another process.

The variation of the potential as hydrogen is gradually removed from the “nickel” electrode during oxidation is shown schematically in Fig. 2. This figure shows that both the  $\text{H}_2\text{NiO}_2$  and  $\text{HNiO}_2$  phases are vario-stoichiometric. About 0.25 electrons (and thus 0.25 protons) per mole can be removed from the nominal “ $\text{H}_2\text{NiO}_2$ ” phase before the onset of the two-phase  $\text{H}_2\text{NiO}_2/\text{HNiO}_2$  equilibrium [24]. Translated to the crystallographic picture, this means that the proton concentration of the  $\text{H}_2\text{NiO}_2$  phase can deviate significantly from the stoichiomet-

ric value, up to a proton vacancy fraction of some 12.5%. The proton-deficient composition limit of the “ $\text{H}_2\text{NiO}_2$ ” phase can thus be expressed as  $\text{H}_{(1.75)}\text{NiO}_2$ .

The relatively long two-phase constant-potential plateau extends from the hydrogen-deficient concentration limit in the “ $\text{H}_2\text{NiO}_2$ ” phase ( $\text{H}_{(1.75)}\text{NiO}_2$ ) to the maximum hydrogen concentration in the “ $\text{HNiO}_2$ ” phase. According to Barnard et al. [2] this is when about 0.75 electrons (or protons) per mole are removed from the electrode. This is equivalent to a composition of  $\text{H}_{1.25}\text{NiO}_2$ . Under more oxidizing conditions, when further hydrogen ions are deleted, the potential of the “ $\text{HNiO}_2$ ” phase gradually becomes more positive over a wide range of composition.

The apparent length of the constant potential two-phase plateau that is observed experimentally depends upon when the electronically conducting  $\text{HNiO}_2$  phase reaches the electrolyte/electrode interface, and thus upon the thickness of the  $\text{H}_2\text{NiO}_2$  and the geometric shape of the  $\text{H}_2\text{NiO}_2/\text{HNiO}_2$  interface. A flat interface is inherently unstable during the oxidation reaction, and the current density is a critical parameter.

During the normal operation of the electrode on this potential plateau the reaction involves the  $\beta$  versions of the structures of the two phases,  $\text{H}_2\text{NiO}_2$  and  $\text{HNiO}_2$ . They both have the brucite type structure, consisting of a hexagonal planar arrangement of oxide ions with octahedrally coordinated  $\text{Ni}^{2+}$  ions between alternate layers. Protons reside between the  $\text{NiO}_2$  layers, two  $\text{H}^+$  ions per  $\text{Ni}^{2+}$  in  $\text{H}_2\text{NiO}_2$ , and one  $\text{H}^+$  per  $\text{Ni}^{3+}$  in the  $\text{HNiO}_2$ . The interlamellar distance is 4.6 Å.

Under more oxidizing conditions, when only the  $\text{HNiO}_2$  phase is present, the electrode is black and an electronically conducting mixed conductor. This phase has wide ranges of both composition and potential. As mentioned above, the upper limit of proton concentration has been found to be approximately  $\text{H}_{1.25}\text{NiO}_2$  for the  $\beta$  modification. Upon further oxidation in the “ $\text{HNiO}_2$ ” regime the gallery proton concentration is reduced.

As shown in Fig. 2, another constant potential plateau will be reached upon further charging the electrode. When this higher potential plateau is reached, oxygen gas starts to evolve. This is generally described as overcharging, and it is found that the  $\text{HNiO}_2$  is gradually changed from the  $\beta$  to the  $\gamma$  structural version when this occurs. This transition has been observed many times [7,16,25], but the details of the crystal structure of  $\gamma$   $\text{HNiO}_2$  are not always the same. In some cases it is called amorphous, but in others it is described as a layer structure containing water or water-solvated alkaline ions that have substituted for some of the protons. In cases in which the  $\gamma$  structure has been determined, it has been reported to have an interlamellar distance of about 7 Å.

A number of authors have shown that the length of the lower plateau observed upon discharging is a function of the amount of the  $\gamma$  formed during overcharging [10]. However, other authors [12] have shown that it is possible to prevent the formation of the  $\gamma$  phase during overcharging by using a dilute electrolyte. Yet the lower discharge potential plateau still appears. There is also evidence that the  $\gamma$  phase can disappear upon extensive overcharging, but the lower discharge plateau is still observed [10].

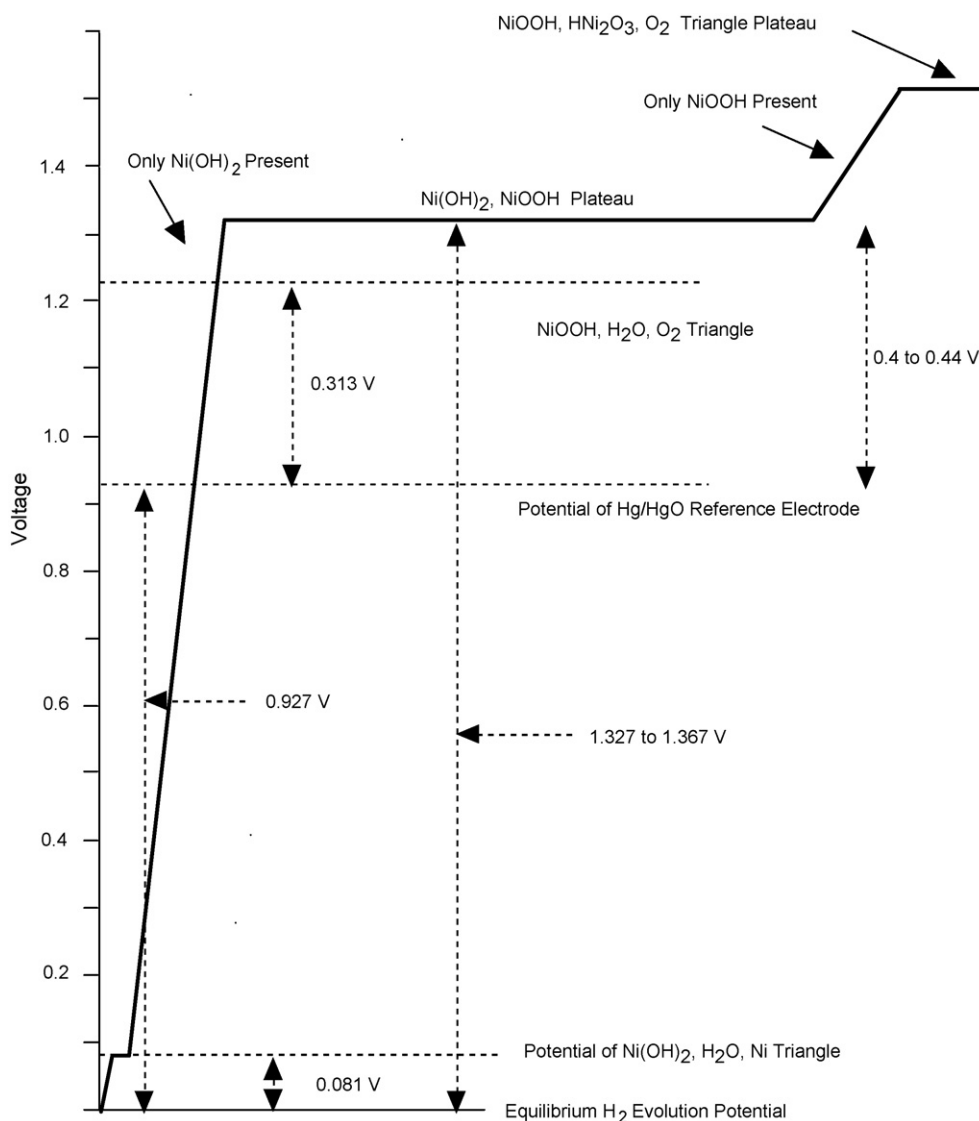


Fig. 2. Variation of the potential as hydrogen is removed from the “nickel” electrode during oxidation when the cell is being charged.

Recent neutron diffraction studies [15], which see only crystalline structures, showed a gradual transition between the  $\gamma$  and  $\beta$  structures upon discharge, with no discontinuity at the transition between the upper and lower discharge plateaus. There was no evidence of a change in the compositions of either of the two phases, just a variation in their amounts, which changed continuously along both discharge plateaus. These authors attributed the presence of the lower plateau to undefined “technical parameters”.

Several other authors have explained the presence of the lower discharge plateau in terms of the formation of some type of barrier layer [2,8], and there is evidence for the formation of  $\beta$   $\text{H}_2\text{NiO}_2$ , which is not electronically conducting, on the lower plateau [13]. This can, of course, be interpreted as a barrier.

These studies all seem to assume that the oxygen that is formed during operation upon the upper plateau during charging comes only from decomposition of the aqueous electrolyte. However, something else is obviously happening that leads to the formation of the lower plateau that is observed upon discharge.

It must also relate to a change in the amounts, compositions or structure of the solid phase, or phases, present.

Although the electrochemical behavior of the “nickel” electrode upon the lower potential plateau can be understood in terms of a pseudo-binary insertion/extraction hydrogen reaction, the evolution of oxygen and the formation of the second discharge plateau indicate that the assumption that the oxygen comes from (only) the electrolysis of the aqueous electrolyte during overcharge cannot be correct. In order to understand this behavior, recognition must be given to the fact that the evolution of oxygen indicates that this electrode should be treated as a ternary H–Ni–O system, rather than as a simple binary.

An approach that has been used successfully over many years to understand the relationship between structural observations, compositions and electrode potentials in ternary systems involves the interpretation of available thermodynamic data in terms of isothermal ternary phase equilibria, and their depiction in what are generally called “Gibbs triangles”. An early example of this, having to do with the electrochemical behav-

ior of lithium-transition metal oxides of interest as positive electrode reactants in lithium battery systems was presented in Ref. [26].

A ternary phase diagram can be simplified by assuming that the phases present have narrow ranges of composition, and can be represented by points at their nominal compositions on the Gibbs triangle. In this case, it is preferable to use the term “phase stability diagram”, instead of “phase diagram”.

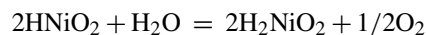
To determine the ternary phase stability diagram relevant to the “nickel” electrode, the first step is to locate the stable phase compositions on the H–Ni–O triangle. The total area of the overall triangle must be divided into sub-triangles. This is done by connecting pairs of phases by drawing two-phase tie lines. Thus all phases lie at the corners of one or more sub-triangles.

All compositions within a given sub-triangle consist of different amounts of the same three corner phases, and have the same electrochemical potential. Thus there is a potential plateau when the overall composition passes through a sub-triangle. As the composition transits a phase at a sub-triangle corner, the potential is composition-dependent, and moves between the values of the two adjacent triangles.

In order to draw the correct sub-triangles for a given ternary system, it is necessary to determine the proper two-phase equilibrium tie lines. An important rule is that tie lines cannot cross.

Use of the Gibbs triangle as a “thinking tool” to understand the basic reactions in the H–Ni–O system has been discussed in several places [19–21]. The major features of the lower-potential portion of this system can be readily determined from available thermodynamic information.

As an example, consider the question whether there is a tie line between  $\text{HNiO}_2$  and  $\text{H}_2\text{O}$ . That is, is  $\text{HNiO}_2$  stable in the presence of water? The alternative is a tie line between  $\text{H}_2\text{NiO}_2$  and oxygen. Only one of these can be stable, for they cross. The answer is decided by calculating the Gibbs free energy change involved in the determining reaction from information on the Gibbs free energy of formation of these phases. This reaction is



and the relevant data are included in Table 1. The result is found to be  $-21.26$  kJ, so the reaction tends to go to the right, which means that the  $\text{HNiO}_2$ – $\text{H}_2\text{O}$  tie line is not stable, and that there is a stable three-phase equilibrium triangle involving  $\text{H}_2\text{NiO}_2$ ,  $\text{HNiO}_2$  and oxygen. A situation in which both  $\text{H}_2\text{NiO}_2$  and  $\text{HNiO}_2$  are both in contact with water can only be metastable.

Table 1  
Values of the Gibbs free energy of formation per mole at 25 °C

Phase	$\Delta G_f^\circ$ (25 °C)	Comments
$\text{H}_2\text{NiO}_2$	–458.6	
$\text{HNiO}_2$	–329.4	
$\text{H}_2\text{O}$	–237.1	
$\text{NiO}$	–211.5	
$\text{NiO}_2$	–215.1	Unstable
$\text{Ni}_2\text{O}_3$	–469.7	Unstable
$\text{Ni}_3\text{O}_4$	–711.9	
$\text{HNi}_2\text{O}_3$	–520.0	

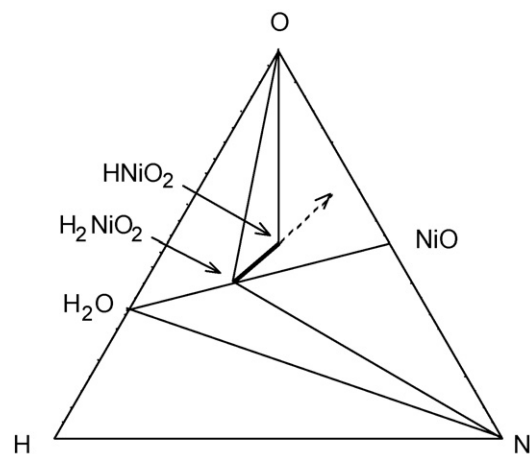


Fig. 3. Partial Gibbs triangle. The main charge–discharge reaction takes place along the thick line. The overall composition moves along the dashed line upon further charging.

A major part of the Gibbs triangle for this system is shown in Fig. 3.

It is seen that the two phases  $\text{H}_2\text{NiO}_2$  and  $\text{HNiO}_2$  are on a tie line that points to the hydrogen corner. Thus neither hydrogen insertion or deletion involve any change in the Ni/O<sub>2</sub> ratio, and these can be considered to be pseudo-binary reactions.

The tie line between those two phases is one side of a triangle that has pure oxygen at its other corner. This means that both of these phases are stable in oxygen, as is well known.

As the result of the Gibbs phase rule, movement of the overall composition along this tie line occurs at a constant potential plateau. It can be calculated from the data in Table 1 that the potential of this plateau is 1.34 V versus pure hydrogen.

Thus the equilibrium electrode potential of the basic  $\text{H}_2\text{NiO}_2$ – $\text{HNiO}_2$  reaction is not only composition-independent, but also more positive than the potential of the decomposition of water. This is what is experimentally observed. Also, because the  $\text{H}_2\text{NiO}_2$  that is between the  $\text{HNiO}_2$  and the water is a solid electrolyte, there is little or no oxygen evolution. This was shown in Fig. 2.

As additional hydrogen is removed the potential moves up the curve where only “ $\text{HNiO}_2$ ” is present. When the overall composition exceeds the stability range of that phase it moves further from the hydrogen corner and enters another region in the phase diagram, as indicated by the dashed line in Fig. 3.

The potential then moves along the upper charging (or overcharging) plateau shown in Fig. 2. Since all of the area within a Gibbs triangle must be divided into sub-triangles, the overall composition must be moving into a new sub-triangle. One corner of this new triangle must be  $\text{HNiO}_2$ , and another must be oxygen. This is consistent with the observation that oxygen is evolved at this higher charging potential. The question is then, where is the third corner?

If gaseous oxygen is evolved from the electrode, not just from decomposition of the water, the third-corner composition must be below (i.e. have less oxygen) than all compositions along the dashed line.

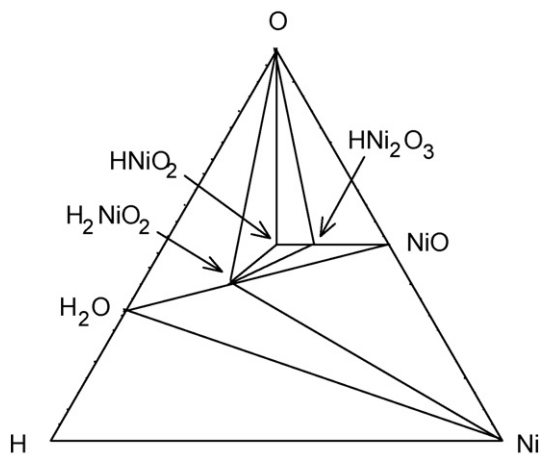


Fig. 4. Gibbs triangle showing the presence of the  $\text{HNi}_2\text{O}_3$  phase.

One possibility might be the phase  $\text{Ni}_3\text{O}_4$ , another could be  $\text{NiO}$ . However, neither of these phases, which readily crystallize, has been observed. There must be another phase with a reduced ratio of oxygen to nickel.

Although not generally recognized by workers in this field, it has been found [27–29] that a phase with a composition close to  $\text{HNi}_2\text{O}_3$  can be formed under conditions comparable to those during charging the electrode on the upper voltage plateau. This phase forms as an amorphous product during the oxidation of  $\text{HNiO}_2$ . Its crystal structure and composition were determined after hydrothermal crystallization. In addition, the mean nickel oxidation state was found by active oxygen analysis to be only 2.65.

The composition  $\text{HNi}_2\text{O}_3$  lies on a line connecting  $\text{HNiO}_2$  and  $\text{NiO}$ . This would then lead to a sub-triangle as shown in Fig. 4, which meets the requirement that there be another phase in equilibrium with both  $\text{HNiO}_2$  and oxygen that has a reduced ratio of oxygen to nickel.

The gradual formation of amorphous  $\text{HNi}_2\text{O}_3$  during oxygen evolution upon the upper overcharging plateau, and its influence upon behavior during discharge, is the key element in the memory effect puzzle.

As overcharge continues, oxygen is evolved, and more and more of the  $\text{HNi}_2\text{O}_3$  phase forms. Thus the overall composition of the solid gradually shifts along the line connecting  $\text{HNiO}_2$  and  $\text{HNi}_2\text{O}_3$ .

Upon discharge, the overall composition moves in the direction of the hydrogen corner of the Gibbs triangle. This is indicated by the dashed line in Fig. 5. It is seen that the  $\text{HNi}_2\text{O}_3$  portion of the total solid moves into a different sub-triangle that has  $\text{H}_2\text{NiO}_2$ ,  $\text{HNi}_2\text{O}_3$  and  $\text{NiO}$  at its corners. From the available thermodynamic data one can calculate that the potential in this sub-triangle is 0.78 V versus hydrogen. That is essentially the same as experimentally found for the lower discharge plateau. The larger the amount of  $\text{HNi}_2\text{O}_3$  that has been formed during overcharging, the longer the corresponding lower discharge plateau will be. The upper discharge plateau becomes correspondingly shorter.

After traversing this triangle, the overall composition of what had been  $\text{HNi}_2\text{O}_3$  moves into another sub-triangle that has

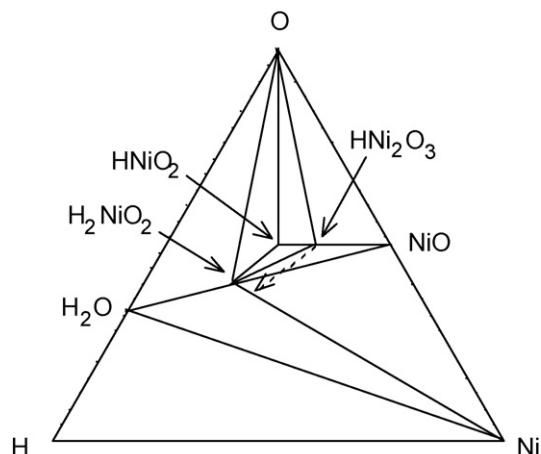


Fig. 5. Composition path during the discharge of the  $\text{HNi}_2\text{O}_3$  formed during overcharge.

$\text{H}_2\text{NiO}_2$ ,  $\text{NiO}$  and  $\text{Ni}$  at its corners. The  $\text{HNi}_2\text{O}_3$  disappears, and the major product is  $\text{H}_2\text{NiO}_2$ . The potential in this sub-triangle can be calculated to be 0.19 V versus hydrogen.

If the electrode is now recharged, its potential does not go back up to the 0.8 V plateau, since  $\text{HNi}_2\text{O}_3$  is no longer present, but goes to the potential for the oxidation of its major component,  $\text{H}_2\text{NiO}_2$ . The overall composition again moves away from the hydrogen corner, and the  $\text{H}_2\text{NiO}_2$  loses hydrogen and gets converted to  $\text{HNiO}_2$ . This is the standard charging cycle low potential plateau. This also means that the lower reduction plateau is no longer active, for the  $\text{HNi}_2\text{O}_3$  has disappeared, and the “memory effect” has been cured.

The calculated potentials in the various sub-triangles of the H–Ni–O system are shown in Fig. 6. The reactions in the H–Ni–O system obviously have very rapid kinetics, for this electrode can be both charged and discharged at high rates. Therefore, it is quite reasonable to expect the phases present to be at or near their equilibrium amounts and compositions. This

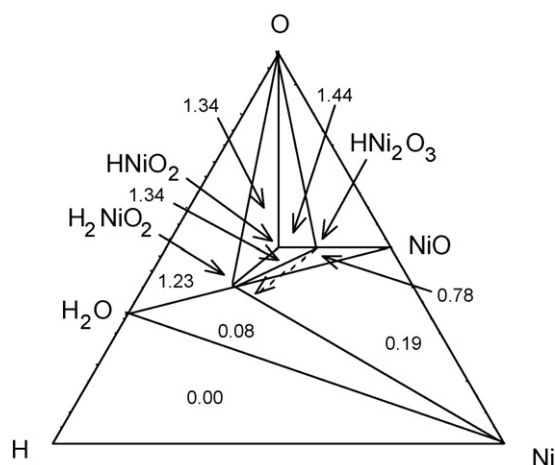


Fig. 6. Calculated values of the potential in the various sub-triangles in the H–Ni–O ternary system vs. hydrogen. It is seen how the composition path during discharge of  $\text{HNi}_2\text{O}_3$  leads to the observation of the lower discharge plateau at about 0.78 V, and the disappearance of that phase when the potential moves to a much lower value.



is indicated by the very good correlation between experimental results and the information obtained by the use of ternary phase stability diagrams based upon the available thermodynamic data.

### 3. Conclusions

The basic mechanisms that are involved in causing the memory effect have been identified. The key element is the formation of an amorphous  $\text{HNi}_2\text{O}_3$  phase upon overcharging into the potential range where oxygen is evolved. Upon subsequent reduction the presence of this phase produces the potential plateau at about 0.8 V versus hydrogen, reducing the available capacity at the normal higher reduction potential. The more the overcharge, the more  $\text{HNi}_2\text{O}_3$  that is formed, and the longer the lower plateau. If the electrode undergoes further reduction this phase disappears, and the potential drops to a much lower value. Subsequent charging of the electrode brings the composition back to the initial state, and the “memory effect” is cured.

This model provides an understanding of the main features of the memory effect, and also explains the several confusing and apparently contradictory observations in the literature. It is hoped that further experimental work will address this matter. Additional confirmation of the presence of  $\text{HNi}_2\text{O}_3$  in the microstructures of overcharged electrodes would be especially useful.

The implication from this mechanism is that the major reason for the memory effect, which is a decrease in the capacity at the normal discharge potential, is related to extensive overcharging, rather than to the use of shallow discharge cycles.

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