



(72) FETCENKO, MICHAEL A., US

(72) FIERRO, CRISTIAN, US

(72) OVSHINSKY, STANFORD R., US

(72) SOMMERS, BETH, US

(72) REICHMAN, BENJAMIN, US

(72) YOUNG, KWO, US

(72) MAYS, WILLIAM, US

(71) OVONIC BATTERY COMPANY, INC., US

(51) Int.Cl.<sup>6</sup> H01M 4/36, H01M 10/38

(30) 1998/08/17 (09/135,460) US

(54) **MATERIAU POUR ELECTRODE POSITIVE COMPOSITE ET  
SON PROCEDE DE FABRICATION**

(54) **COMPOSITE POSITIVE ELECTRODE MATERIAL AND  
METHOD FOR MAKING SAME**

(57) A composite positive electrode material for use in electrochemical cells. The composite material may comprise a particle of positive electrode material, and a conductive material at least partially embedded within the particle of positive electrode material. The material may comprise a particle of positive electrode material, and a nucleating particle at least partially embedded therein.

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b>  <b>H01M 4/36, 10/38</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/10212</b>  <b>(43) International Publication Date:</b> 24 February 2000 (24.02.00)
<b>(21) International Application Number:</b> PCT/US99/18164  <b>(22) International Filing Date:</b> 11 August 1999 (11.08.99)  <b>(30) Priority Data:</b> 09/135,460                      17 August 1998 (17.08.98)                      US  <b>(71) Applicant:</b> OVONIC BATTERY COMPANY, INC. [US/US]; 1707 Northwood, Troy, MI 48084 (US).  <b>(72) Inventors:</b> FETCENKO, Michael, A.; 429 Daylily Drive, Rochester Hills, MI 48307 (US). FIERRO, Cristian; 17075 White Haven, Northville, MI 48167 (US). OVSHINSKY, Stanford, R.; 2700 Squirrel Road, Bloomfield Hills, MI 48013 (US). SOMMERS, Beth; 6062 Waterfront Drive, Waterford, MI 48329 (US). REICHMAN, Benjamin; 3740 Macnichol Trail, West Bloomfield, MI 48323 (US). YOUNG, Kwo; 4131 Morehead Drive, Troy, MI 48098 (US). MAYS, William; 14850 Arcola, Livonia, MI 48154 (US).  <b>(74) Agents:</b> SCHLAZER, Philip, H. et al.; Energy Conversion Devices, Inc., 1675 W. Maple Road, Troy, MI 48084 (US).		<b>(81) Designated States:</b> AU, BR, CA, JP, KR, MX, NO, RU, SG, UA, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> COMPOSITE POSITIVE ELECTRODE MATERIAL AND METHOD FOR MAKING SAME  <b>(57) Abstract</b>  A composite positive electrode material for use in electrochemical cells. The composite material may comprise a particle of positive electrode material, and a conductive material at least partially embedded within the particle of positive electrode material. The material may comprise a particle of positive electrode material, and a nucleating particle at least partially embedded therein.		

0

**COMPOSITE POSITIVE ELECTRODE MATERIAL**  
**AND METHOD FOR MAKING SAME**

**FIELD OF THE INVENTION**

5

The instant invention relates generally to positive electrode materials for rechargeable batteries such as nickel hydroxide materials. More specifically, the instant invention relates to composite nickel hydroxide particulate having increased conductivity over the prior art material.

10

**BACKGROUND OF THE INVENTION**

15

In rechargeable alkaline cells, weight and portability are important considerations. It is also advantageous for rechargeable alkaline cells to have long operating lives without the necessity of periodic maintenance. Rechargeable alkaline cells are used in numerous consumer devices such as calculators, portable radios, and cellular phones. They are often configured into a sealed power pack that is designed as an integral part of a specific device. Rechargeable alkaline cells can also be configured as larger cells that can be used, for example, in industrial, aerospace, and electric vehicle applications.

20

25

There are many known types of Ni based cells such as nickel cadmium ("NiCd"), nickel metal hydride ("Ni-MH"), nickel hydrogen, nickel zinc, and nickel iron cells. NiCd rechargeable alkaline cells are the most widely used although it appears that they will be replaced by Ni-MH cells. Compared to NiCd cells, Ni-MH cells made of synthetically engineered materials have superior performance parameters and contain no toxic elements.

30

35

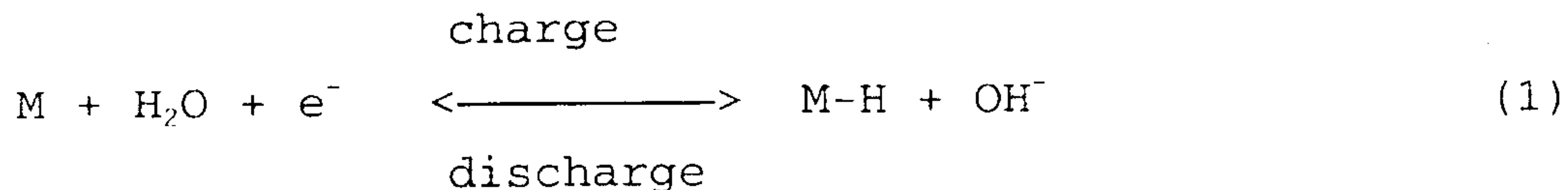
Ni-MH cells utilize a negative electrode that is capable of the reversible electrochemical storage of hydrogen. Ni-MH cells usually employ a positive electrode of nickel hydroxide material. The negative and positive electrodes are spaced apart in the alkaline electrolyte. Upon application of an electrical potential across a Ni-MH cell, the Ni-MH material of the negative electrode is charged by the electrochemical



WO 00/10212

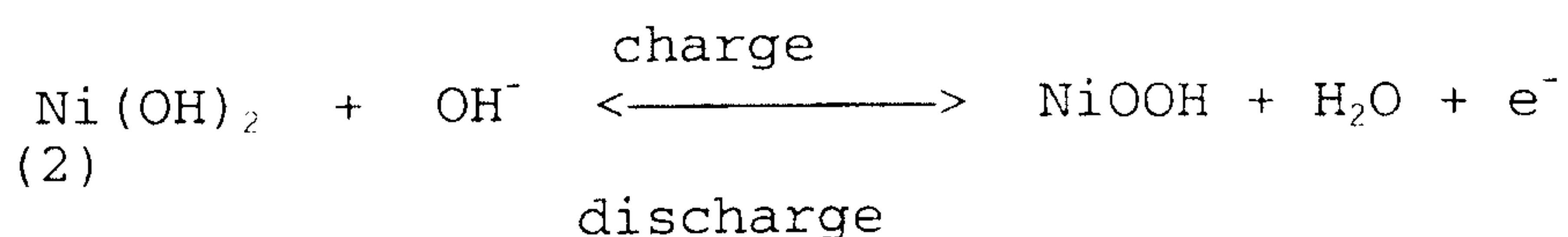
PCT/US99/18164

0 absorption of hydrogen and the electrochemical discharge of  
a hydroxyl ion, as shown in equation (1):



5

The negative electrode reactions are reversible. Upon  
discharge, the stored hydrogen is released to form a water  
molecule and release an electron. The reactions that take  
place at the nickel hydroxide positive electrode of a Ni-MH  
10 cell are shown in equation (2):



15

Ni-MH materials are discussed in detail in U.S. Patent No.  
5,277,999 to Ovshinsky, et al., the contents of which are  
incorporated by reference.

20

25

In alkaline rechargeable cells, the discharge capacity of  
a nickel based positive electrode is limited by the amount of  
active material, and the charging efficiencies. The charge  
capacities of a Cd negative electrode and a MH negative  
electrode are both provided in excess, to maintain the optimum  
capacity and provide overcharge protection. Thus, a goal in  
making the nickel positive electrode is to obtain as high an  
energy density as possible. The volume of a nickel hydroxide  
positive electrode is sometimes more important than weight.  
The volumetric capacity density is usually measured in mAh/cc  
and specific capacity is written as mAh/g.

30

At present, sintered or pasted nickel hydroxide positive  
electrodes are used in NiCd and Ni-MH cells. The process of  
making sintered electrodes is well known in the art.

WO 00/10212

PCT/US99/18164

0 Conventional sintered electrodes normally have an energy density of around 480-500 mAh/cc. In order to achieve significantly higher capacity, the current trend has been away from sintered positive electrodes and toward foamed and pasted electrodes.

5 Sintered nickel electrodes have been the dominant nickel electrode technology for several decades for most applications. These consist of a porous nickel plaque of sintered high surface area nickel particles impregnated with nickel hydroxide active material either by chemical or  
10 electrochemical methods. While expensive, sintered electrodes provide high power, high reliability, and high cycle life, but not the highest energy density. They are likely to remain important for high reliability military and aerospace applications for some time.

15 Pasted nickel electrodes consist of nickel hydroxide particles in contact with a conductive network or substrate, preferably having a high surface area. There have been several variants of these electrodes including the so-called plastic-bonded nickel electrodes which utilize graphite as a  
20 microconductor and also including the so-called foam-metal electrodes which utilize high porosity nickel foam as a substrate loaded with spherical nickel hydroxide particles and cobalt conductivity enhancing additives. Pasted electrodes of the foam-metal type now dominate the consumer market due to  
25 their low cost, simple manufacturing, and higher energy density relative to sintered nickel electrodes.

WO 00/10212

PCT/US99/18164

0           Conventionally, the nickel battery electrode reaction has  
been considered to be a one electron process involving  
oxidation of divalent nickel hydroxide to trivalent nickel  
oxyhydroxide on charge and subsequent discharge of trivalent  
nickel oxyhydroxide to divalent nickel hydroxide, as shown in  
5           equation 2 hereinbelow.

          Some recent evidence suggests that quadrivalent nickel is  
involved in the nickel hydroxide redox reaction. This is not  
a new concept. In fact, the existence of quadrivalent nickel  
was first proposed by Thomas Edison in some of his early  
10          battery patents. However, full utilization of quadrivalent  
nickel has never been investigated.

          In practice, electrode capacity beyond the one-electron  
transfer theoretical capacity is not usually observed. One  
reason for this is incomplete utilization of the active  
15          material due to isolation of oxidized material. Because  
reduced nickel hydroxide material has a high resistance, the  
reduction of nickel hydroxide adjacent the current collector  
forms a less conductive surface that interferes with the  
subsequent reduction of oxidized active material that is  
20          farther away.

          As discussed in U.S. Patent No. 5,348,822, nickel  
hydroxide positive electrode material in its most basic form  
has a maximum theoretical specific capacity of 289 mAh/g, when  
one charge/discharge cycles from a  $\beta$ II phase to a  $\beta$ III phase  
25          and results in one electron transferred per nickel atom. It  
was recognized in the prior art that greater than one electron  
transfer could be realized by deviating from the  $\beta$ II and  $\beta$ III



WO 00/10212

PCT/US99/18164

0 limitations and cycling between a highly oxidized  $\gamma$ -phase  
nickel hydroxide phase and the  $\beta$ II phase. However, it was  
also widely recognized that such gamma phase nickel hydroxide  
formation destroyed reversible structural stability and  
therefore cycle life was unacceptably degraded. A large  
5 number of patents and technical literature disclosed  
modifications to nickel hydroxide material designed to inhibit  
and/or prevent the destructive formation of the transition to  
the  $\gamma$ -phase, even though the higher attainable capacity  
through the use of  $\gamma$ -phase is lost.

10 Attempts to improve nickel hydroxide positive electrode  
materials began with the addition of modifiers to compensate  
for what was perceived as the inherent problems of the  
material. The use of compositions such as NiCoCd, NiCoZn,  
NiCoMg, and their analogues are described, for example, in the  
15 following patents:

U.S. Patent No. Re. 34,752, to Oshitani, et al., reissued  
4 October 1994, describes a nickel hydroxide active material  
that contains nickel hydroxide containing 1-10wt% zinc or 1-3  
wt% magnesium to suppress the production of gamma-NiOOH. The  
20 invention is directed toward increasing utilization and  
discharge capacity of the positive electrode. Percent  
utilization and percent discharge capacity are discussed in  
the presence of various additives.

Oshitani, et al. describe the lengths that routineers in  
25 the art thought it was necessary to go to in order to inhibit  
 $\gamma$ -NiOOH. The patent states:

Further, since the current  
density increased in accordance

0 with the reduction of the  
specific surface area, a large  
amount of higher oxide  $\gamma$ -NiOOH  
may be produced, which may  
5 cause fatal phenomena such as  
stepped discharge  
characteristics and/or  
swelling. The swelling due to  
the production of  $\gamma$ -NiOOH in  
10 the nickel electrode is caused  
by the large change of the  
density from high density  $\beta$ -  
NiOOH to low density  $\gamma$ -NiOOH.  
The inventors have already  
15 found that the production of  $\gamma$ -  
NiOOH can effectively be  
prevented by addition of a  
small amount of cadmium in a  
solid solution into the nickel  
hydroxide. However, it is  
20 desired to achieve the  
substantially same or more  
excellent effect by utilizing  
additive other than the cadmium  
from the viewpoint of the  
25 environmental pollution."

U.S. Patent No. 5,366,831, to Watada, et al., issued 22  
November 1994, describes the addition of a single Group II  
element (such as Zn, Ba, and Co) in a solid solution with  
30 nickel hydroxide active material. The Group II element is  
described as preventing the formation of gamma phase nickel  
hydroxide thereby reducing swelling, and the cobalt is  
described as reducing the oxygen overvoltage thereby  
increasing high temperature charging efficiency. Both oxygen  
35 overvoltage and charge efficiency are described as increasing  
with increasing cobalt.

U.S. Patent No. 5,451,475, to Ohta, et al., issued 19  
September 1995, describes the positive nickel hydroxide  
electrode material as fabricated with at least one of the  
40 following elements added to the surface of the particles



WO 00/10212

PCT/US99/18164

0       thereof: cobalt, cobalt hydroxide, cobalt oxide, carbon  
powder, and at least one powdery compound of Ca, Sr, Ba, Cu,  
Ag, and Y. The cobalt, cobalt compound, and carbon are  
described as constituents of a conductive network to improve  
charging efficiency and conductivity. The powdery compound is  
5       described as adsorbed to the surface of the nickel hydroxide  
active material where it increases the overvoltage, for  
evolution of oxygen, thereby increasing nickel hydroxide  
utilization at high temperature. Ohta, et al. claims that  
increased utilization in NiMH cells using the disclosed  
10       invention remains constant up to a high number of  
charge/discharge cycles and utilization does not drop as much  
at higher temperatures as it does in cells that do not embody  
the invention.

U.S. Patent No. 5,455,125 to Matsumoto, et al., issued 3  
15       October 1995, describes a battery having a positive electrode  
comprising nickel hydroxide pasted on a nickel foam substrate  
with solid solution regions of Co and salts of Cd, Zn, Ca, Ag,  
Mn, Sr, V, Ba, Sb, Y, and rare earth elements. The addition  
of the solid solution regions is intended to control the  
20       oxygen overvoltage during charging. The further external  
addition of "electric conducting agents" such as powdered  
cobalt, cobalt oxide, nickel, graphite, "and the like," is  
also described. Energy density is shown as constant at 72  
Wh/kg at 20°C and 56 Wh/kg at 45°C for embodiments of the  
25       invention over the life of the NiMH cell.

U.S. Patent No. 5,466,543, to Ikoma, et al., issued 14  
November 1995, describes batteries having improved nickel

WO 00/10212

PCT/US99/18164

0 hydroxide utilization over a wide temperature range and  
increased oxygen overvoltage resulting from the incorporation  
of at least one compound of yttrium, indium, antimony, barium,  
or beryllium, and at least one compound of cobalt or calcium  
into the positive electrode. Cobalt hydroxide, calcium oxide,  
5 calcium hydroxide, calcium fluoride, calcium peroxide, and  
calcium silicate are specifically described compounds.  
Additionally described additives are cobalt, powdery carbon,  
and nickel. The specification particularly describes AA cells  
using a positive electrode containing 3 wt% zinc oxide and 3  
10 wt% calcium hydroxide as superior in terms of cycle life (250  
cycles at 0°C, 370 cycles at 20°C, and 360 cycles at 40°C) and  
discharge capacity (950 mAh at 20°C, 850 mAh at 40°C, and 780  
mAh at 50°C).

U.S. Patent No. 5,489,314, to Bodauchi, et al., issued 6  
15 February 1996, describes mixing the nickel hydroxide positive  
electrode material with a cobalt powder compound followed by  
an oxidation step to form a beta cobalt oxyhydroxide on the  
surface of the nickel hydroxide powder.

U.S. Patent No. 5,506,070, to Mori, et al., issued 9  
20 April 1996, describes nickel hydroxide positive electrode  
material containing 2-8 wt% zinc mixed with 5-15% cobalt  
monoxide. The zinc reduces swelling and the cobalt increases  
utilization. The capacity of the resulting electrode is  
stated as being "improved up to 600 mAh/cc" without further  
25 description.

U.S. 5,571,636, to Ohta, et al., issued 5 November 1996,  
describes the addition of at least one powdery compound of Ca,



WO 00/10212

PCT/US99/18164

0 Sr, Ba, Cu, Ag, and Y to the surface of nickel hydroxide  
active positive electrode material. This patent states that  
these compounds are adsorbed to the surface of the nickel  
hydroxide active material creating a conductive network that  
increases the oxygen overvoltage and improves utilization of  
5 the active material at high temperatures. Increased  
utilization in NiMH cells using the '636 invention remains  
constant up to a large number of cycles and utilization does  
not drop as much at higher temperatures as it does in cells  
that do not embody the invention.

10 In all of the prior art, the basic nickel hydroxide  
material is treated, most commonly, by the addition of a  
single element, usually Co compounds, to increase electrical  
conductivity and usually one other element, usually Cd or Zn,  
to suppress and/or prevent  $\gamma$ -phase formation. The mechanisms  
15 for the asserted improvements in all the above patents are  
attributable to the following effects:

1. Improved speed of activation, resistance to poisons,  
and marginal capacity improvement via increased utilization.  
At the present time, most commercial nickel metal hydride  
20 batteries achieve these effects through the external addition  
of up to 5 wt% cobalt and/or cobalt-containing compound. It  
is generally believed that the major reason cobalt is  
effective at these levels is because it creates an extensive  
external conductive network independent of the nickel  
25 hydroxide material. Frequently, powdered carbon, powdered  
cobalt metal, and powdered nickel metal are also added to  
create separate conductive networks and thereby improve



WO 00/10212

PCT/US99/18164

0 utilization. Of course, a major drawback of increasing the  
amount of such additives is that the amount of active nickel  
hydroxide electrode material is correspondingly reduced,  
thereby reducing capacity. Further, since Co is expensive,  
the addition of even minimum amounts of Co greatly increases  
5 cost.

2. Cycle life is extended by decreasing swelling that is  
initiated by density changes between the oxidized and reduced  
states of the nickel hydroxide material. Swelling, in turn,  
is accelerated by the uncontrolled density changes between  
10  $\beta$ II- $\beta$ III phase nickel hydroxide and  $\alpha$ - $\gamma$  or  $\beta$ II- $\gamma$  phase nickel  
hydroxide. Cd and Zn incorporated into the nickel hydroxide  
effectively reduce the swelling by reducing the difference in  
density in the charged and discharged material and increasing  
the mechanical stability of the nickel hydroxide material  
15 itself. This is accomplished by promoting oxygen evolution  
and thereby reducing charge acceptance which prevents the  
nickel hydroxide material from attaining the highly oxidized  
state (the  $\gamma$ -phase state). However, by suppressing or at  
least significantly inhibiting  $\gamma$ -phase formation, the nickel  
20 hydroxide is limited to transferring no more than one electron  
per Ni atom. Further, in order to effectively inhibit  $\gamma$ -phase  
nickel hydroxide, it is necessary to employ a relatively high  
wt% of the inhibitor element such as Zn or Cd, which high  
percentage results in a greatly reduced amount of active  
25 material being present thereby resulting in reduced  
electrochemical capacity.

WO 00/10212

PCT/US99/18164

0           3.    The aforementioned "safety release" mechanism of  
oxygen evolution to avoid highly oxidized states of nickel  
hydroxide material actually is an impediment to high  
temperature operation because a significant increase in the  
rate of oxygen evolution occurs with increasing temperature.  
5   The effect of such increased oxygen evolution is a very  
substantial decrease in utilization and ultimately a reduction  
in energy storage at higher temperatures in the NiMH battery  
using these materials. At 55°C, for example, run times of a  
battery may be reduced by 35-55% compared to the room  
10   temperature performance of that battery.

Elevated operational temperature conditions aside, none  
of these prior art modifications result in more than an  
incremental improvement in performance and none result in a  
significant increase in the capacity of the nickel hydroxide  
15   material itself, even at room temperature. Further, these  
modifications fail to address the special operational  
requirements of NiMH batteries, particularly when NiMH  
batteries are used in electric vehicles, hybrid vehicles,  
scooters and other high capacity, high drain rate  
20   applications. Because NiMH negative electrodes have been  
improved and now exhibit an extremely high storage capacity,  
the nickel hydroxide positive electrode material is  
essentially the limiting factor in overall battery capacity.  
This makes improving the electrochemical performance of the  
25   nickel hydroxide material in all areas more important than in  
the past. Unfortunately, the elements currently added to the  
nickel hydroxide material result in insufficient improvements



WO 00/10212

PCT/US99/18164

0 in performance before competing deleterious mechanisms and  
effects occur. For example, Cd cannot be used in any  
commercial battery because of the environmental impact  
thereof, and Co and Zn appear to become most effective only at  
levels that result in a significant decrease in cell capacity;  
5 more specifically, energy per electrode weight.

Ovshinsky and his team have developed positive electrode  
materials that have demonstrated reliable transfer of more  
than one electron per nickel atom. Such materials are  
described in U.S. Patent No. 5,344,728 and 5,348,822 (which  
10 describe stabilized disordered positive electrode materials)  
and copending U.S. Patent Application No. 08/300,610 filed  
August 23, 1994, and U.S. Patent Application No. 08/308,764  
filed September 19, 1994.

Previously all of the work on nickel hydroxide positive  
15 electrode material has concentrated on improving it's  
conductivity in two ways. First electrically conductive  
additives have been externally mixed with the nickel hydroxide  
materials used to produce pasted electrodes. Such additives  
include Co, CoO, Ni, Cu, and C. The additives are generally  
20 in the form of powder, fibers or the like. These techniques  
have achieved moderate success in that Ni-MH batteries have  
achieved impressive gains in high rate discharge performance.  
However, there are two remaining problems. First, the  
emergence of hybrid electric vehicles has demanded that Ni-MH  
25 batteries achieve 1000 W/kg of power. Conventional electric  
vehicle batteries achieve 250 W/kg and special designs achieve  
500-600 W/kg. Second, even present power levels are achieved



WO 00/10212

PCT/US99/18164

0 by a very expensive and elaborate positive electrode  
embodiment (i.e., an expensive foam metal skeleton and  
expensive use of cobalt compounds).

The second way in which artisans have increased the  
conductivity of nickel hydroxide is by co-precipitating cobalt  
5 hydroxide along with nickel hydroxide to increase it's  
internal conductivity. While NiCo co-precipitates have better  
conductivity and utilization than pure nickel hydroxide, the  
improvement can only be considered incremental with no room  
for further improvement.

10 The two methods discussed above, while increasing the  
power and capacity of the nickel hydroxide materials and  
electrodes have still not realized the full potential thereof.  
As stated above, there is still a need for significant gains  
in power and high rate discharge capability. Therefore, there  
15 is a need in the art for additional improvements in the  
conductivity of positive electrode materials and,  
specifically, in the conductivity of nickel hydroxide for use  
in rechargeable battery applications.

20

#### SUMMARY OF THE INVENTION

An objective of the present invention is to provide an  
active material for a positive electrode having increased  
25 conductivity. This and other objectives are satisfied by a  
composite positive electrode material for use in  
electrochemical cells. The material comprises a particle of

WO 00/10212

PCT/US99/18164

0 positive electrode material; and a conductive material at  
least partially embedded within the particle of positive  
electrode material. The conductive material may be metallic  
particles such as nickel particles.

5 This and other objectives are satisfied by a method for  
producing a composite positive electrode material comprising  
a particle of positive electrode material and a conductive  
material at least partially embedded within the particle of  
positive electrode material, the method comprising the step  
of: combining a metal ion solution, a caustic solution, and a  
10 conductive material, whereby a precipitation solution  
including the composite positive electrode material is formed.  
The combining step may comprise the steps of mixing the  
conductive material with the metal ion solution to form a  
suspension; and mixing the suspension with the caustic  
15 solution.

This and other objectives are also satisfied by a  
composite positive electrode material comprising: a particle  
of positive electrode material; and a nucleating particle at  
least partially embedded within the particle of positive  
20 electrode material.

This and other objectives are also satisfied by a method  
for producing a composite positive electrode material  
comprising particles of positive electrode material having  
nucleating particles at least partially embedded therein, the  
25 method comprising the step of: combining a metal ion solution,  
a caustic solution, and the nucleating particles, whereby a  
precipitation solution including the composite positive

WO 00/10212

PCT/US99/18164

0 electrode material is formed. The combining step may  
comprise the steps of: mixing the metal ion solution and the  
nucleating particles, thereby forming a suspension of the  
nucleating particles in the metal ion solution; and mixing the  
caustic solution with the suspension.

5

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a photomicrograph, at magnification of  
10,000x, of an embodiment of the composite material of the  
present invention;

10 Figure 2 is a stylized drawing of an embodiment of the  
composite material where the conductive material is in the  
form of a conductive network;

Figure 3 shows complex impedance plots for positive  
electrodes comprising nickel hydroxide material formed with  
15 and without embedded nickel particles; and

Figure 4 shows discharge curves for positive electrodes  
comprising nickel hydroxide material formed with and without  
embedded nickel particles.

20

#### DETAILED DESCRIPTION OF THE INVENTION

The instant inventors have discovered improvements in  
positive electrode material for use in electrochemical cells  
25 and methods for making the improved materials. Disclosed  
herein is a composite positive electrode material for use in  
electrochemical cells. Generally, the composite positive



WO 00/10212

PCT/US99/18164

0 electrode material comprises a particle of positive electrode material, and a conductive material which is at least partially embedded within the particle of positive electrode material. The conductive material may be totally embedded within the particle of positive electrode material.

5 Generally, the conductive material is any material which is electrically conductive. Preferably, the conductive material is chosen so that the conductivity of the composite positive electrode material is greater than the conductivity of the active positive electrode material alone.

10 The conductive material may comprise a metal. Examples of metals which may be used include, but are not limited to, nickel, nickel alloys, copper, and copper alloys. Preferably, the metal is nickel. As used herein, "nickel" refers to substantially pure nickel. Also, as used herein, "copper" refers to substantially pure copper.

15 It is noted that nickel has an atomic configuration comprising d-orbitals. While not wishing to be bound by theory, it is believed that the d-orbitals may effect the active positive electrode material surrounding the nickel material.

20 The conductive material may also comprise a material selected from the group consisting of oxides, nitrides, carbides, silicides, and borides. The conductive material may comprise carbon, or graphite. The conductive material may comprise copper oxide, cobalt oxide, or indium tin oxide.

25 The conductive material may be in the form of at least one conductive particle which is at least partially embedded

WO 00/10212

PCT/US99/18164

0 in the particle of positive electrode material. Preferably,  
the conductive particle is metallic. More preferably, the  
conductive particle is a nickel particle. Figure 1 shows a  
photomicrograph, at magnification of 10,000x, of an embodiment  
of the composite material of the present invention. In this  
5 embodiment, the composite material comprises a particle of  
positive electrode material 1, and a nickel particle 3 which  
is totally embedded in the particle of positive electrode  
material 1.

The conductive material may comprise a plurality of  
10 conductive particles which are at least partially embedded  
within the particle of positive electrode material. The  
plurality of conductive particles may be isolated from one  
another. Alternately, at least some of the particles may be  
touching others so as to form a conductive network of  
15 particles.

The conductive particles may have a variety of shapes and  
sizes. For example, the particles may be substantially  
spherical. Alternately, the particles may be elongated  
wherein one dimension is longer than another dimension. For  
20 example, the particles may be ellipsoidal or cylindrical. As  
well, the particles may be in the form of threadlike fibers.  
These elongated particles may have an average length which is  
less than or equal to about 10 microns. As well they may have  
an average diameter of less than or equal to about 1.0 micron.  
25 These sizes are merely reference points and may be varied  
within the scope of the invention. An example of conductive  
particles are the INCO T-210 nickel particles. The INCO T-210



WO 00/10212

PCT/US99/18164

0 nickel particles have a particle morphology with an average  
sub-micron Fisher diameter of about .9 microns, an apparent  
density of about .6 grams per cm<sup>3</sup>, and a BET of about 1.75  
m<sup>2</sup>/g.

5 The conductive material may take the form of a conductive  
network. The conductive network may have various topologies.  
One example of a conductive network is a lattice structure  
which may be formed by the interconnection of conductive  
particles, fibers, strands, and the like. Another example  
of a conductive network is the branching tree-like structure  
10 that is shown in Figure 2. The conductive network 3A branches  
out throughout the active positive electrode particle 1.  
Another example of a conductive network is one comprising one  
or more carbon nanotubes and/or fullerenes.

15 While not wishing to be bound by theory, the inventors  
believe that the embedded conductive material, such as the  
nickel particle 3 shown in Figure 1, serves one or both of two  
possible roles in the composite material. First, the  
inventors believe that the conductive material serves as an  
electronically conductive pathway through the active positive  
20 electrode material, thereby increasing the useable capacity of  
the active material. The internal conductive pathway also  
improves the ionic transport within the active material and  
prevents portions of the active material from becoming  
electrically isolated by reducing the transport distance  
25 through the active material and/or optimizing alignment of  
crystallite pathways.



WO 00/10212

PCT/US99/18164

0           The present inventors believe that one factor that limits  
the nickel electrode reaction to capacities equivalent to one  
electron or less is the underutilization of the nickel  
hydroxide active material. It is believed that the  
underutilization is caused by electronic isolation of oxidized  
5 nickel oxyhydroxide (NiOOH) material by the formation of  
highly resistive nickel hydroxide (Ni(OH)<sub>2</sub>) material adjacent  
to the active material, and by poor transport of ions to the  
inner portions of the electrode which are remote from the  
electrolyte. The present invention, overcomes such electronic  
10 isolation and ionic transport limitations. Hence, in this  
invention, electronic isolation of the active material is  
reduced or avoided by providing an electronically conductive  
pathway in the interior of the nickel hydroxide particles.  
This allows for added electronic pathways which reduce or  
15 prevent isolation of the active material by the more resistive  
reduced nickel hydroxide material.

          The second role that the conductive material, such as the  
nickel particle 3, may play is that of a nucleation site for  
the growth of nickel hydroxide crystallites. The particles  
20 of nickel hydroxide material comprise crystallites, and the  
nickel particle 3 behaves as a "nucleating particle" (i.e., a  
nucleation site for the growth of the nickel hydroxide  
crystallites). As a nucleation site, the nickel particle 3  
may orient the nickel hydroxide crystallites as they deposit  
25 onto the nickel particle during precipitation. Furthermore,  
the nickel particle 3 may also influence the size and/or shape  
of the nickel hydroxide crystallites. Each nickel hydroxide

WO 00/10212

PCT/US99/18164

0 particle is composed of many very fine crystallites which may  
have an improved crystallographic orientation within the  
boundary of the crystallite.

5 The protonic conductivity (i.e., the conductivity of  
protons) in a typical nickel hydroxide particle is dominated  
by (1) conduction within crystallites and (2) conduction  
across the grain boundaries between adjacent crystallites.  
When the crystallite size is too large, the fully discharged  
nickel hydroxide does not have enough vacancies, created at  
the grain boundaries for the initial charging current to  
10 provide for a proton to hop from one vacancy to another  
vacancy, and therefore such large crystallites provide for  
relatively poor conductivity. When the crystallite size is  
too small, the adjacent crystal lattice conduction networks  
will not be aligned due to the presence of too many grain  
15 boundary vacancies for the protons to hop across and protonic  
conductivity is thereby impeded. There exists an optimum  
crystallite size in which the proper number of grain boundary  
vacancies are present. In these latter materials, sufficient  
vacancies are present for proper inter-crystallite  
20 conductivity to occur and the protons have sufficient room to  
follow the proper conductive path through the crystallite it  
then enters.

In addition to the proper crystallite size of the nickel  
hydroxide material, the crystallites are believed to require  
25 proper orientation to be highly conductive. That is, if there  
are discontinuities in the crystallite orientation from one  
crystallite to another then the crystallites that are



WO 00/10212

PCT/US99/18164

0       improperly oriented for lower resistance current flow will  
dominate the resistance of the material. Conversely, if all  
of the crystallites are properly oriented, the conductivity of  
the nickel hydroxide material may be increased. The inventors  
believe that the nickel particle 3 may preferentially orient  
5       the crystallites of nickel hydroxide in this highly conductive  
orientation as they deposit, such that the nickel hydroxide  
has a higher protonic conductivity than nickel hydroxide  
deposited in a random manner.

Thus, it is possible that the addition of nucleation  
10       sites alter the size and/or shape of the crystallites. In a  
random precipitation, it might be expected that crystallites  
would have a spherical shape, while in the present invention  
the crystallites could have a more elongated shape. While not  
wishing to be bound by theory, it is possible that protonic  
15       conduction is preferential along the 101 axis of the nickel  
hydroxide. The role of the nucleation sites could be to  
reduce the distance along the 101 plane to the crystallite  
boundary or to orient the 101 planes from one crystallite to  
an other for enhance conduction.

20       Hence, an alternate embodiment of the present invention,  
is a composite positive electrode material comprising a  
particle of active positive electrode material (such as nickel  
hydroxide), and a "nucleating particle" which is at least  
partially embedded within the particle of positive electrode  
25       material. The nucleating particle does not have to be an  
electrically conductive material. Instead, the nucleating  
particle need only provide a nucleation site for the growth of



WO 00/10212

PCT/US99/18164

0     crystallites forming from the positive electrode material. As  
discussed above, the addition of nucleation sites may orient  
the deposited crystallites of the positive electrode material  
such that the conductivity of the material is increased. The  
nucleation sites may provide for the proper deposition surface  
5     to orient the crystallites as well as to determine the average  
size and/or shape of the crystallites so as to increase the  
conductivity of the material.

      The nucleating particles are not limited to any specific  
shape, size or topology. Examples of shapes include, but not  
10    limited to, substantially spherical, substantially flat,  
elongated, cylindrical, ellipsoidal, fiber-like, cubic,  
parallelopiped, etc. As well, the surfaces of the nucleating  
particles may be varied to effect the growth of the positive  
electrode material crystals. For example, the nucleating  
15    particles may be partially etched to provide either a  
roughened surface or an oxide free surface.

      Further, it may also be possible to provide a "nucleation  
structure" having a more complex topology than a single  
nucleating particle and which also acts as a surface for the  
20    growth of crystals of positive electrode material. For  
example, the nucleation structure may be a plurality of  
connected nucleating particles. The nucleation structure may  
have the form of a lattice such as a matrix, screen or foam.  
The nucleation structure may have a topology similar to that  
25    of the conductive network shown in Figure 2. As well, the  
nucleation structure may have a topology sufficient to  
increase the conductivity of the positive electrode material

WO 00/10212

PCT/US99/18164

0 by appropriately orienting the growth of the crystals and/or  
appropriately determining the size of the crystals and/or the  
shape of the crystals.

The active positive electrode material used in the  
present invention may be may be any type of positive electrode  
5 material known in the art. Examples include nickel hydroxide  
material and manganese hydroxide material. It is within the  
spirit and intent of this invention that any and all kinds of  
nickel hydroxide, or positive materials in general, may be  
used. Even pure nickel hydroxide without cobalt, a material  
10 with poor conductivity for commercial application, may be  
transformed into a viable positive electrode material via the  
internally embedded nickel particles or fibers described  
herein.

The nickel hydroxide material may be a disordered  
15 material. The use of disordered materials allow for permanent  
alteration of the properties of the material by engineering  
the local and intermediate range order. The general  
principals are discussed in U.S. Patent No. 5,348,822, the  
contents of which are incorporated by reference herein. The  
20 nickel hydroxide material may be compositionally disordered.  
"Compositionally disordered" as used herein is specifically  
defined to mean that this material contains at least one  
compositional modifier and/or a chemical modifier. Also, the  
nickel hydroxide material may also be structurally disordered.  
25 "Structurally disordered" as used herein is specifically  
defined to mean that the material has a conductive surface and  
filamentous regions of higher conductivity, and further, that



WO 00/10212

PCT/US99/18164

0 the material has multiple or mixed phases where alpha, beta, and gamma-phase regions may exist individually or in combination.

5 The nickel hydroxide material may comprise a compositionally and structurally disordered multiphase nickel hydroxide host matrix which includes at least one modifier chosen from the group consisting of Al, Ba, Bi, Ca, Co, Cr, Cu, F, Fe, In, K, La, Li, Mg, Mn, Na, Nd, Pb, Pr, Ru, Sb, Sc, Se, Sn, Sr, Te, Ti, Y, and Zn. Preferably, the nickel hydroxide material comprises a compositionally and structurally disordered multiphase nickel hydroxide host matrix which includes at least three modifiers chosen from the group consisting of Al, Ba, Bi, Ca, Co, Cr, Cu, F, Fe, In, K, La, Li, Mg, Mn, Na, Nd, Pb, Pr, Ru, Sb, Sc, Se, Sn, Sr, Te, Ti, Y, and Zn. These embodiments are discussed in detail in 10 commonly assigned U.S. Patent No. 5,637,423 the contents of which is incorporated by reference herein.

20 The nickel hydroxide materials may be multiphase polycrystalline materials having at least one gamma-phase that contain compositional modifiers or combinations of compositional and chemical modifiers that promote the multiphase structure and the presence of gamma-phase materials. These compositional modifiers are chosen from the group consisting of Al, Bi, Co, Cr, Cu, Fe, In,  $\text{LaH}_3$ , Mg, Mn, Ru, Sb, Sn,  $\text{TiH}_2$ ,  $\text{TiO}$ , Zn. Preferably, at least three 25 compositional modifiers are used. The nickel hydroxide materials may include the non-substitutional incorporation of at least one chemical modifier around the plates of the



WO 00/10212

PCT/US99/18164

0 material. The phrase "non-substitutional incorporation around the plates", as used herein means the incorporation into interlamellar sites or at edges of plates. These chemical modifiers are preferably chosen from the group consisting of Al, Ba, Ca, Co, Cr, Cu, F, Fe, K, Li, Mg, Mn, Na, Sr, and Zn.

5 As a result of their disordered structure and improved conductivity, the nickel hydroxide materials do not have distinct oxidation states such as  $2^+$ ,  $3^+$ , or  $4^+$ . Rather, these materials form graded systems that pass 1.0 to 1.7 and higher electrons.

10 The nickel hydroxide material may comprise a solid solution nickel hydroxide material having a multiphase structure that comprises at least one polycrystalline gamma-phase including a polycrystalline gamma-phase unit cell comprising spacedly disposed plates with at least one chemical  
15 modifier incorporated around said plates, said plates having a range of stable intersheet distances corresponding to a  $2^+$  oxidation state and a  $3.5^+$ , or greater, oxidation state; and at least three compositional modifiers incorporated into the solid solution nickel hydroxide material to promote the  
20 multiphase structure. This embodiment is fully described in commonly assigned U.S. Patent No. 5,348,822, the contents of which is incorporated by reference herein.

25 Preferably, one of the chemical modifiers is chosen from the group consisting of Al, Ba, Ca, Co, Cr, Cu, F, Fe, K, Li, Mg, Mn, Na, Sr, and Zn. The compositional modifiers may be chosen from the group consisting of a metal, a metallic oxide, a metallic oxide alloy, a metal hydride, and a metal hydride

WO 00/10212

PCT/US99/18164

0 alloy. Preferably, the compositional modifiers are chosen  
from the group consisting of Al, Bi, Co, Cr, Cu, Fe, In, LaH<sub>3</sub>,  
Mn, Ru, Sb, Sn, TiH<sub>2</sub>, TiO, and Zn. In one embodiment, one of  
the compositional modifiers is chosen from the group  
consisting of Al, Bi, Co, Cr, Cu, Fe, In, LaH<sub>3</sub>, Mn, Ru, Sb,  
5 Sn, TiH<sub>2</sub>, TiO, and Zn. In another embodiment, one of the  
compositional modifiers is Co. In an alternate embodiment,  
two of the compositional modifiers are Co and Zn. The nickel  
hydroxide material may contain 5 to 30 atomic percent, and  
preferable 10 to 20 atomic percent, of the compositional or  
10 chemical modifiers described above.

The disordered nickel hydroxide electrode materials may  
include at least one structure selected from the group  
consisting of (i) amorphous; (ii) microcrystalline; (iii)  
polycrystalline lacking long range compositional order; and  
15 (iv) any combination of these amorphous, microcrystalline, or  
polycrystalline structures. A general concept of the present  
invention is that a disordered active material can more  
effectively accomplish the objectives of multi-electron  
transfer, stability on cycling, low swelling, and wide  
20 operating temperature than prior art modifications.

Also, the nickel hydroxide material may be a structurally  
disordered material comprising multiple or mixed phases where  
alpha, beta, and gamma-phase region may exist individually or  
in combination and where the nickel hydroxide has a conductive  
25 surface and filamentous regions of higher conductivity.

Additional improvement of the nickel hydroxide material  
of the present invention are possible when these disordered



WO 00/10212

PCT/US99/18164

0 materials are combined with electrolytes where the electrolyte  
comprises at least one element chosen from the group  
consisting of Ba, Ca, Cs, K, Li, Na, Ra, Rb, and Sr, combined  
with at least one member of the group consisting of Br, Cl, F,  
OH. Particular examples of such electrolytes are formulations  
5 of KOH, NaOH, LiOH and/or CsF, and KOH and CsOH.

Also disclosed herein is a method for producing a  
composite positive electrode material comprising a particle of  
positive electrode material, and a conductive material at  
10 least partially embedded within the particle of positive  
electrode material. The general method for making the  
composite material is by precipitation of a positive electrode  
material (such as the nickel hydroxide material) onto the  
conductive material suspended in a precipitation bath. The  
15 specific method can be varied widely, as will be described  
hereinbelow, as long as the positive electrode material is  
deposited onto the conductive material.

The method requires a source of metal ion solution, a  
source of the conductive material, and a source of caustic  
20 (sodium hydroxide) be provided. Generally, the method  
comprises the step of combining the metal ion solution, the  
caustic solution and the conductive material so that a  
precipitation solution which includes the composite positive  
electrode material is formed.

25 A major proportion of the metal ion solution should  
include the active materials main metal ion, for instance  
nickel ions, for deposition of a nickel hydroxide material.



WO 00/10212

PCT/US99/18164

0 While nickel ions are typically used, manganese ions (for  
deposition of a manganese hydroxide solution) may also be  
used. Also, other metal ions may be added to the metal ion  
solution to modify and enhance the performance of the nickel  
hydroxide material. The metal ion solution may further  
5 comprise one or more metal ions selected from the group  
consisting of Al, Ba, Bi, Ca, Co, Cr, Cu, Fe, In, K, La, Li,  
Mg, Mn, Na, Nd, Pb, Pr, Ru, Sb, Sc, Se, Sn, Sr, Te, Ti, Y, and  
Zn. The metal ion solution may be selected from the group  
consisting of a metal sulfate solution, a metal nitrate  
10 solution, and mixtures thereof.

The caustic solution is generally a very concentrated  
sodium hydroxide solution, and is standard in the art of  
nickel hydroxide precipitation. As with prior art  
precipitation processes, the sodium hydroxide can be partially  
15 replaced by hydroxides of other alkali metal hydroxides, as  
long as they are soluble.

In one embodiment, the method of producing the composite  
material comprises the step of mixing the conductive material  
with the metal ion solution to form a suspension. The  
20 suspension is then mixed with the caustic solution in a  
reactor vessel. Hence, in this embodiment, the conductive  
material is suspended in the metal ion solution before being  
mixed with the caustic.

The conductive material is preferably nickel particles  
25 (which may be fibers). It is noted that while the remaining  
discussion of the method of making the composite material is

WO 00/10212

PCT/US99/18164

0 in terms of nickel particles, all types of conductive materials (as discussed hereinabove) may be used.

Once suspended in the metal ion solution, the nickel particles act as nucleation sites for the precipitation of the positive electrode active material (hereinafter nickel  
5 hydroxide material). After the suspension is formed, the caustic solution is then mixed with the suspension to precipitate the nickel hydroxide material onto the nickel particle, thereby forming the deposit. As the nickel hydroxide deposits onto the nickel particle, the nickel  
10 particle becomes at least partially embedded in the nickel hydroxide material.

The inventors have noted the preferred aspect of adding the nickel particles to the reactor vessel by first suspending the nickel particles in the metal ion solution, especially  
15 when the metal ion solution is predominately a nickel sulfate solution. When added in this manner, nucleation and precipitation proceeded excellently. In an earlier trial (in which the metal ion solution was also predominately a nickel sulfate solution) the nickel particles were added  
20 independently to the reactor vessel. This case was unsuccessful, resulting in clumped metallic nickel particles outside of the nickel hydroxide. While not wishing to be bound by theory, the inventors believe that suspending the nickel particles in the metal ion solution may be preferred  
25 due to the acidic nature of the sulfate solution. It may be that the nickel particles are partially etched, providing either a roughened surface or an oxide free surface better for



WO 00/10212

PCT/US99/18164

0 nucleation. When ammonium hydroxide is added to form a nickel  
ammonia complex (discussed below), it is also possible that  
the nickel ammonia complex which forms just prior to or  
simultaneous with the precipitation assists or promotes the  
desirable nucleation. It is still possible that direct  
5 introduction of the nickel particles to the precipitation  
reactor could work through the use of a wetting agent or other  
means.

In another embodiment of the method, a source of ammonium  
hydroxide is also provided. The ammonium hydroxide is mixed  
10 with the metal ion solution to form an amine complex with the  
metal ions. The amine complex is then reacted with the  
caustic solution to form the nickel hydroxide material. The  
step of mixing the ammonium hydroxide solution with the metal  
ion solution may occur before or concurrent with the step of  
15 mixing the metal ion solution and the nickel particles. The  
step of mixing the ammonium hydroxide solution with the metal  
ion solution may also occur after the step of mixing the metal  
ion solution and the nickel particles, but before the step of  
mixing the caustic solution with the suspension. Finally, the  
20 step of mixing the ammonium hydroxide solution with the metal  
ion solution may occur concurrent with the step of mixing the  
caustic solution with the suspension.

The method of the present invention may further comprise  
the step of separating the composite positive electrode  
25 material from the precipitation solution. The composite  
positive electrode material may be washed with deionized water  
and/or caustic solution.



WO 00/10212

PCT/US99/18164

0           The concentrations of the solutions are variable and  
generally known in the art. The nickel particles may form  
about 0.1% to about 35% by weight of the final nickel  
hydroxide powder. Present results indicate that the effect of  
the added nickel particles can be seen to start at about 2% by  
5           weight of nickel particles. After about 20% by weight, the  
reduction in active material is not compensated for by either  
the increase in conductivity or the decrease in isolated  
active material. More preferably, the nickel particles form  
about 2% to about 10% by weight of the nickel hydroxide  
10          powder.

#### Example

A composite nickel hydroxide material was prepared by  
mixing a metal ion solution, a calcium nitrate solution, a  
15          caustic solution of NaOH, and an ammonium hydroxide solution  
in a reactor vessel.

The metal ion solution was prepared by adding 177 grams  
of  $\text{CoSO}_4$ , 15.5 grams  $\text{MgSO}_4$  and 11.2 grams of  $\text{ZnSO}_4$  to 0.058  
gallons of water and 1.25 gallons of  $\text{NiSO}_4$  solution. About  
20          50 grams of the INCO T-210 nickel powder was added to the  
metal ion solution as a source of metallic nickel particles  
and continuously stirred.

The metal ion solution is added to the reactor vessel at  
a rate of about 0.058 gallons per hour. A solution of 66%  
25          calcium nitrate is concurrently added to the reactor vessel at  
a rate of about 0.0025 gallons per hour. Ammonium hydroxide  
is added to the reaction vessel at a rate of about 0.016

WO 00/10212

PCT/US99/18164

0 gallons per hour. Finally, a caustic solution comprising  
about 0.96 gallons of a 6.5M solution of NaOH is added to  
reaction vessel at a rate which is sufficient to keep the pH  
of the reaction vessel at about 11.3.

5 The reaction vessel is kept at a temperature of about  
60°C and is stirred at a rate of about 670 revolution per  
minute. The quantities of metal ion solution, calcium  
nitrate, caustic, and ammonium hydroxide used are sufficient  
to produce about 1 Kg of the composite nickel hydroxide  
material over a 24 hour period of time. After the composite  
10 nickel hydroxide material is formed, it is rinsed with  
deionized water or dilute caustic, and dried.

Also disclosed herein is a method for producing a  
composite positive electrode material comprising particles of  
15 active positive electrode material having nucleating particles  
at least partially embedded therein. The method comprises the  
step of combining a metal ion solution, a caustic solution,  
and the nucleating particles, whereby a precipitation solution  
including the composite positive electrode material is formed.  
20 In general, the method for producing the composite positive  
electrode material with nucleating particles is the same as  
the method discussed above with regards to using the  
conductive material. Nucleating particles (which need not be  
conductive) are used instead of the conductive material. Of  
25 course, the nucleating particles may be electrically  
conductive particles such as nickel particles.



WO 00/10212

PCT/US99/18164

0           Figure 3 shows the AC impedance measurements for positive  
electrodes comprising two different positive electrode  
materials. In general, the AC impedance measurements of a  
positive electrode is a plot showing the real portion of  
electrode impedance on the horizontal axis and the imaginary  
5       portion of electrode impedance on the vertical axis. The  
impedances are plotted as a function of a range of frequencies  
starting at a high frequency of about 10 kHz and going to a  
low frequency of about 20 uHz.

          Referring to Figure 3, Plot A is the AC impedance  
10       measurements of a positive electrode comprising a nickel  
hydroxide active material. Plot B is the AC impedance  
measurement of a positive electrode comprising the composite  
positive electrode material of the present invention. The  
composite material comprises the same nickel hydroxide active  
15       material (from which Plot A was made) with the addition of  
about 5% by weight of embedded nickel particles. A n  
important electrical parameter of a battery electrode is the  
"charge transfer resistance",  $R_{CT}$ . The charge transfer  
resistance is calculated from the nyquist plot describing the  
20       AC impedance of the electrode over a range of frequencies.

          The charge transfer resistance corresponds to the  
diameter of the "high frequency semicircle" of the AC  
impedance plot multiplied by the number of grams of positive  
electrode material. Referring to Figure 3, this diameter is  
25       denoted as Diam(A) for Plot A and Diam(B) for Plot B. The  
Diam(A) was measured to be about .113 ohms while the number of  
grams of the positive electrode material (nickel hydroxide



WO 00/10212

PCT/US99/18164

0 without embedded nickel) was about 2.85 grams. Hence, the  
charge transfer resistance  $R_{CT}(A)$  of the nickel hydroxide  
material without embedded nickel was about .322 ohms-gram.

5 The diameter of the semi-circle of Plot B,  $Diam(B)$  was  
measured to be about .062 ohms while the number of grams of  
the positive electrode material (the same nickel hydroxide  
material with 5% embedded Ni) was about 2.94 grams. Hence,  
the charge transfer resistance  $R_{CT}(B)$  of the nickel hydroxide  
material with the 5% embedded nickel fibers was about .182  
ohms-gram. Hence, the charge transfer resistance for the  
10 nickel hydroxide material with embedded nickel,  $R_{CT}(B)$ , was  
significantly lower than the charge transfer resistance for  
the nickel hydroxide material without the embedded nickel  
 $R_{CT}(A)$ . The addition of the nickel particles to the nickel  
hydroxide material may lower the charge transfer resistance of  
15 the positive electrode material by over 50%.

Also disclosed herein is a positive electrode material  
characterized by a charge transfer resistance less than about  
.22 ohms-gram. Preferably, the positive electrode material  
has a charge transfer resistance is less than about .20 ohms-  
20 gram. Most preferably, the charge transfer resistance is less  
than about .19 ohms-gram.

Figure 4 shows positive electrode discharge curves A and  
B. The discharge curves A, B show the positive electrode half  
cell potentials relative to an Hg/HgO reference electrode.  
25 The potentials are given from about 95% state of charge to  
about 50% state of charge. Discharge curve A is for a  
positive electrode having an active electrode material which

WO 00/10212

PCT/US99/18164

0 comprises a nickel hydroxide material without any embedded  
nickel particles. Discharge curve B is for a positive  
electrode having an active material comprising the same nickel  
hydroxide material with about 5% by weight of embedded nickel  
fibers (i.e., about 5% of the INCO T-210 nickel particles).  
5 Comparison of the discharge curves shows that the addition of  
the nickel fibers increases the half cell potential of the  
positive electrode over the entire range of state of discharge  
(i.e., from 95% to 50%). Though not wishing to be bound by  
theory, it is believed that the increased potential is at  
10 least partially due to the decreased charge transfer  
resistance discussed above.

Capacity and utilization are also greatly enhanced by the  
present invention. Positive electrodes were prepared for  
half-cell testing by pasting a slurry of about 5% by weight of  
15 Co metal, about 5% by weight of CoO with PVA binder and the  
remainder active material onto foam metal substrates.

The respective electrode samples included approximately  
2 grams of active material paste (including binder and  
external additives, but not including the foam metal  
20 substrate) and were tested in an excess electrolyte  
configuration with the following results. "Sample A" is a  
nickel hydroxide positive electrode material without any  
embedded nickel fibers. "Sample B" is the same nickel  
hydroxide material with about 5% by weight of the embedded  
25 nickel fibers (5% of INCO T-210 nickel particles).  
"Commercial" is a commercially available material. The

WO 00/10212

PCT/US99/18164

0 capacities of the positive electrode materials are shown in  
the Table below.

Table

	<u>Sample</u>	<u>mAh/g</u>
5	Commercial	230
	A (without embedded nickel)	276
	B (with 5% embedded nickel)	292

10 As can be seen from the Table, the inclusion of the 5% nickel  
fibers in the nickel hydroxide material greatly enhances the  
utilization and capacity of the active material.

It is noted that the composite positive electrode  
material of the present invention may provide for a "fully  
pasted positive electrode" that does not use a foam or fiber  
15 skeleton or substrate. Usually, this embodiment is formed  
from a standard nickel hydroxide material with externally  
conductive additives and a plastic binder. The composite  
electrode material of the present invention could provide the  
improved power and rate discharge needed for practical  
20 commercialization of this type of electrode.

The term "substrate" as used herein relates to any  
electrically conductive support for the active positive  
electrode material. It may take the form of a foam, grid,  
plate, foil, expanded metal or any other type of support  
25 structure. It may take the form of conventional nickel foils,  
plates and foams, as well as, carbon networks, fibers or  
particulate and cobalt oxyhydroxide networks. It may be made



WO 00/10212

PCT/US99/18164

0 from any electronically conductive material. Preferably, it  
is made from a metal such as nickel or a nickel alloy. More  
preferably, the substrate for the positive electrode is a  
nickel foam.

5 It is to be understood that the disclosure set forth  
herein is presented in the form of detailed embodiments  
described for the purpose of making a full and complete  
disclosure of the present invention, and that such details are  
not to be interpreted as limiting the true scope of this  
invention as set forth and defined in the appended claims.

10

WO 00/10212

PCT/US99/18164

0 We claim:

1. A composite positive electrode material for use in electrochemical cells, said material comprising:

a particle of positive electrode material; and

5 a conductive material at least partially embedded within said particle of positive electrode material.

2. The composite positive electrode material of claim 1, wherein said conductive material is totally embedded within said particle of positive electrode material.

10

3. The composite positive electrode material of claim 1, wherein said conductive material comprises a metal.

15

4. The composite positive electrode material of claim 1, wherein said conductive material comprises nickel.

5. The composite positive electrode material of claim 1, wherein said conductive material comprises a nickel alloy.

20

6. The composite positive electrode material of claim 1, wherein said conductive material comprises copper.

7. The composite positive electrode material of claim 1, wherein said conductive material comprises a copper alloy.

25



WO 00/10212

PCT/US99/18164

- 0        8.    The composite positive electrode material of claim 1,  
         wherein said conductive material comprises at least one  
         material selected from the group consisting of oxides,  
         nitrides, carbides, silicides, and borides.
- 5        9.    The composite positive electrode material of claim 1,  
         wherein said conductive material comprises at least one  
         material selected from the group consisting of carbon, and  
         graphite.
- 10       10.   The composite positive electrode material of claim 1,  
         wherein said conductive material comprises at least one  
         material selected from the group consisting of copper oxide,  
         cobalt oxide, and indium tin oxide.
- 15       11.   The composite positive electrode material of claim 1,  
         wherein said conductive material comprises at least one  
         particle.
12.   The composite positive electrode material of claim 11,  
20       wherein said at least one particle is elongated.
13.   The composite positive electrode material of claim 11,  
         wherein said at least one particle is substantially spherical.
- 25       14.   The composite positive electrode material of claim 11,  
         wherein said at least one particle is a fiber.

WO 00/10212

PCT/US99/18164

0 15. The composite positive electrode material of claim 11,  
wherein said at least one particle has an average length of  
less than about 10 microns.

16. The composite positive electrode material of claim 11,  
5 wherein said at least one particle has an average diameter of  
less than about 1.0 micron.

17. The composite positive electrode material of claim 1,  
wherein said conductive material comprises a conductive  
10 network.

18. The composite positive electrode material of claim 1,  
wherein said positive electrode material comprises nickel  
hydroxide material.

15 19. The composite positive electrode material of claim 18,  
wherein said nickel hydroxide material comprises a  
compositionally and structurally disordered multiphase nickel  
hydroxide host matrix which includes at least one modifier  
20 chosen from the group consisting of Al, Ba, Bi, Ca, Co, Cr,  
Cu, F, Fe, In, K, La, Li, Mg, Mn, Na, Nd, Pb, Pr, Ru, Sb, Sc,  
Se, Sn, Sr, Te, Ti, Y, and Zn.

20. The composite positive electrode material of claim 19,  
25 wherein said nickel hydroxide material host matrix includes at  
least three modifiers chosen from the group consisting of Al,



WO 00/10212

PCT/US99/18164

0 Ba, Bi, Ca, Co, Cr, Cu, F, Fe, In, K, La, Li, Mg, Mn, Na, Nd,  
Pb, Pr, Ru, Sb, Sc, Se, Sn, Sr, Te, Ti, Y, and Zn.

21. The composite positive electrode material of claim 18,  
wherein said nickel hydroxide material comprises:

5 a solid solution nickel hydroxide material having a  
multiphase structure that comprises at least one  
polycrystalline gamma-phase including a polycrystalline  
gamma-phase unit cell comprising spacedly disposed plates with  
at least one chemical modifier incorporated around said  
10 plates, said plates having a range of stable intersheet  
distances corresponding to a 2<sup>+</sup> oxidation state and a 3.5<sup>+</sup>, or  
greater, oxidation state; and

at least three compositional modifiers incorporated into  
said solid solution nickel hydroxide material to promote said  
15 multiphase structure.

22. The composite positive electrode material of claim 21,  
wherein one of said at least one chemical modifier is chosen  
from the group consisting of Al, Ba, Ca, Co, Cr, Cu, F, Fe, K,  
20 Li, Mg, Mn, Na, Sr, and Zn.

23. The composite positive electrode material of claim 21,  
wherein said at least three compositional modifiers are chosen  
from the group consisting of a metal, a metallic oxide, a  
25 metallic oxide alloy, a metal hydride, and a metal hydride  
alloy.

WO 00/10212

PCT/US99/18164

- 0        24. The composite positive electrode material of claim 21,  
wherein said at least three compositional modifiers are chosen  
from the group consisting of Al, Bi, Co, Cr, Cu, Fe, In, LaH<sub>3</sub>,  
Mn, Ru, Sb, Sn, TiH<sub>2</sub>, TiO, Zn.
- 5        25. The composite positive electrode material of claim 22,  
wherein one of said at least three compositional modifiers is  
chosen from the group consisting of Al, Bi, Co, Cr, Cu, Fe,  
In, LaH<sub>3</sub>, Mn, Ru, Sb, Sn, TiH<sub>2</sub>, TiO, Zn.
- 10       26. The composite positive electrode material of claim 21,  
wherein one of said at least three compositional modifiers is  
Co.
- 15       27. The composite positive electrode material of claim 21,  
wherein two of said at least three compositional modifiers are  
Co and Zn.
- 20       28. The composite positive electrode material of claim 22,  
wherein said at least three compositional modifiers is chosen  
from the group consisting of Al, Bi, Co, Cr, Cu, Fe, In, LaH<sub>3</sub>,  
Mn, Ru, Sb, Sn, TiH<sub>2</sub>, TiO, Zn.
- 25       29. The composite positive electrode material of claim 21,  
wherein said nickel hydroxide material is a disordered  
material and has at least one structure selected from the  
group consisting of (i) amorphous; (ii) microcrystalline;  
(iii) polycrystalline lacking long range compositional order;



WO 00/10212

PCT/US99/18164

0 and (iv) any combination of said amorphous, microcrystalline,  
or polycrystalline structures.

30. The composite positive electrode material of claim 21,  
wherein said nickel hydroxide material is a structurally  
5 disordered material comprising multiple or mixed phases where  
alpha, beta, and gamma-phase regions may exist individually or  
in combination and said nickel hydroxide has a conductive  
surface and filamentous regions of higher conductivity.

10 31. The composite positive electrode material of claim 21,  
wherein said nickel hydroxide material contains 5 to 30 atomic  
percent of said at least three compositional modifiers or said  
at least one chemical modifier and provide electronic  
conductivity.

15 32. The composite positive electrode material of claim 21,  
wherein said nickel hydroxide material contains 10 to 20  
atomic percent of said at least three compositional modifiers  
or said at least one chemical modifier.

20 33. The composite positive electrode material of claim 21,  
wherein said at least three compositional modifiers are  
incorporated into said nickel hydroxide material to disrupt  
the formation of large crystallites.

25 34. A method for producing a composite positive electrode  
material comprising a particle of positive electrode material,

WO 00/10212

PCT/US99/18164

0 and a conductive material at least partially embedded within  
said particle of positive electrode material, said method  
comprising the step of:

combining a metal ion solution, a caustic solution, and  
said conductive material, whereby a precipitation solution  
5 including said composite positive electrode material is  
formed.

35. The method of claim 34, wherein said combining step  
comprises the steps of:

10 mixing said conductive material with said metal ion  
solution to form a suspension; and  
mixing said suspension with said caustic solution.

36. The method of claim 35, wherein said combining step  
15 further comprises the step of:

mixing an ammonium hydroxide solution with said metal ion  
solution to form a metal amine complex solution.

37. The method of claim 36, wherein said mixing said ammonium  
20 hydroxide step occurs before said step of mixing said  
conductive material with said metal ion solution.

38. The method of claim 36, wherein said mixing said ammonium  
hydroxide step occurs concurrently with said step of mixing  
25 said conductive material with said metal ion solution.

WO 00/10212

PCT/US99/18164

0 39. The method of claim 36, wherein said mixing said ammonium hydroxide step occurs after said step of mixing said conductive material and said metal ion solution, but before said step of mixing said caustic solution with said suspension.

5

40. The method of claim 36, wherein said mixing said ammonium hydroxide step occurs concurrent with said step of mixing said caustic solution with said suspension.

10

41. The method of claim 34, wherein said method further comprises the step of separating said composite positive electrode material from said precipitation solution.

15

42. The method of claim 41, wherein said method further comprises the step of washing said composite positive electrode material with deionized water.

20

43. The method of claim 41, wherein said method further comprises the step of washing said composite positive electrode material with caustic solution.

25

44. The method of claim 34, wherein said metal ion solution comprises metal ions of one or more elements selected from the group consisting of nickel ions, and manganese ions.

45. The method of claim 44, wherein said metal ion solution further comprises metal ions of one or more elements selected



WO 00/10212

PCT/US99/18164

0 from the group consisting of Al, Ba, Bi, Ca, Co, Cr, Cu, Fe,  
In, K, La, Li, Mg, Mn, Na, Nd, Pb, Pr, Ru, Sb, Sc, Se, Sn, Sr,  
Te, Ti, Y, and Zn.

46. The method of claim 34, wherein said metal ion solution  
5 is selected from the group consisting of a metal sulfate  
solution, a metal nitrate solution, and mixtures thereof.

47. The method of claim 46, wherein said metal ion solution  
comprises metal ions of one or more elements selected from the  
10 group consisting of Al, Ba, Bi, Ca, Co, Cr, Cu, Fe, In, K, La,  
Li, Mg, Mn, Na, Nd, Pb, Pr, Ru, Sb, Sc, Se, Sn, Sr, Te, Ti, Y,  
and Zn.

48. The method of claim 34, wherein said metal ion solution  
15 comprises nickel ions.

49. The method of claim 34, wherein said metal ion solution  
comprises manganese ions.

20

50. A composite positive electrode material comprising:  
a particle of positive electrode material; and  
a nucleating particle at least partially embedded within  
said particle of positive electrode material.

25

51. The composite positive electrode material of claim 50,  
wherein said nucleating particle orients the crystallites of

WO 00/10212

PCT/US99/18164

0 said particle of positive electrode material so that the conductivity of said material is increased.

52. The composite positive electrode material of claim 50, wherein said nucleating particle determines the average size  
5 of the crystallites of said particle of positive electrode material so that the conductivity of said material is increased.

53. The composite positive electrode material of claim 50, wherein said nucleating particle determines the average shape  
10 of the crystallites of said particle of positive electrode material so that the conductivity of said material is increased.

15 54. A method for producing a composite positive electrode material comprising particles of positive electrode material having nucleating particles at least partially embedded therein, said method comprising the step of:

combining a metal ion solution, a caustic solution, and  
20 said nucleating particles, whereby a precipitation solution including said composite positive electrode material is formed.

55. The method of claim 54, wherein said combining step  
25 comprises the steps of:

WO 00/10212

PCT/US99/18164

0            mixing said metal ion solution and said nucleating  
particles, thereby forming a suspension of said nucleating  
particles in said metal ion solution; and

          mixing said caustic solution with said suspension.

5            56. The method of claim 55, wherein said combinin step  
further comprises the step of:

          mixing an ammonium hydroxide solution with said metal ion  
solution to form a metal amine complex solution.

10           57. A positive electrode material characterized by a charge  
transfer resistance less than about .22 ohms-gram.

          58. The positive electrode material of claim 57, wherein said  
charge transfer resistance is less than about .20 ohms-gram.

15



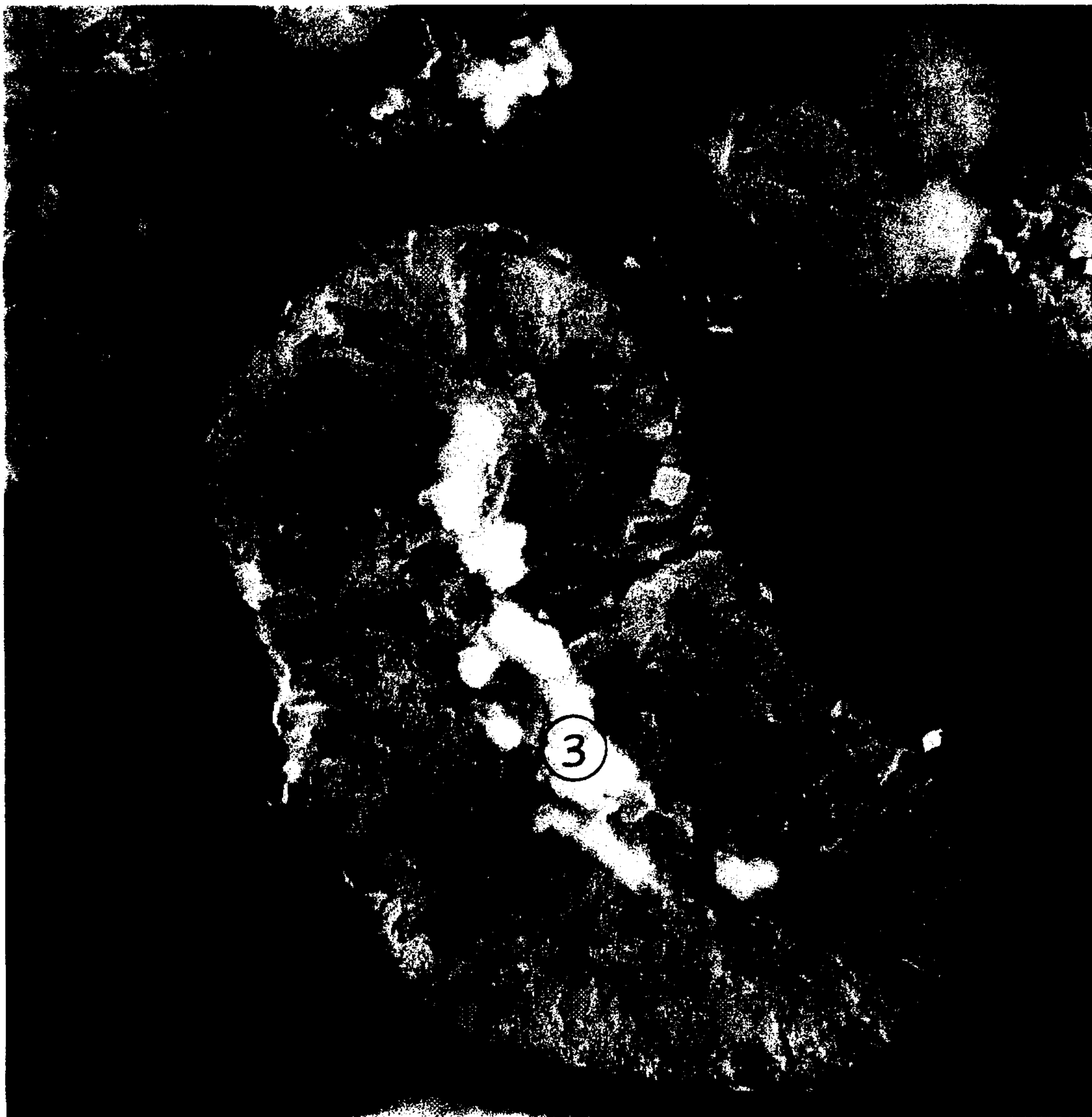


FIG - 1

SUBSTITUTE SHEET (RULE 26)

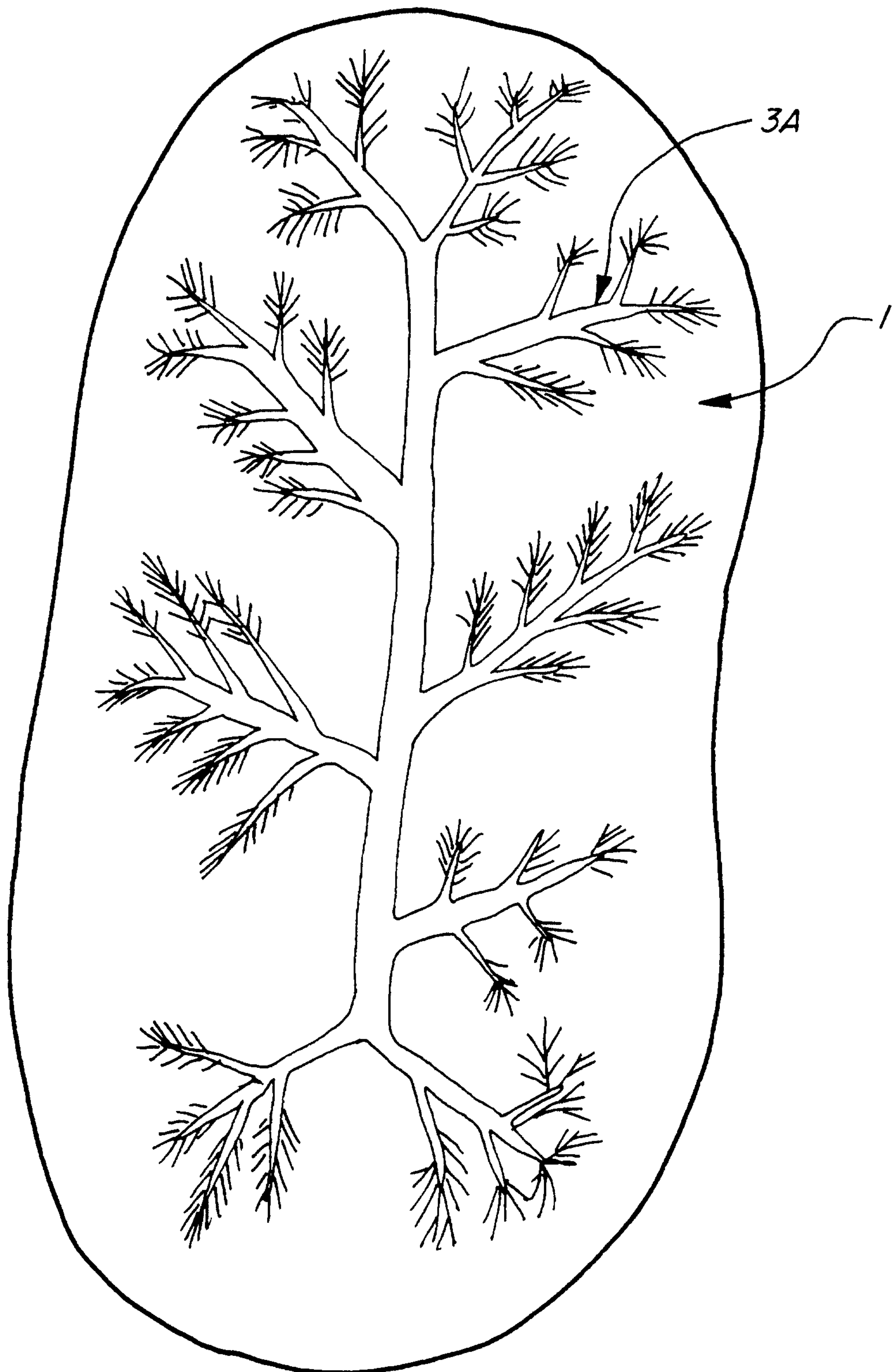
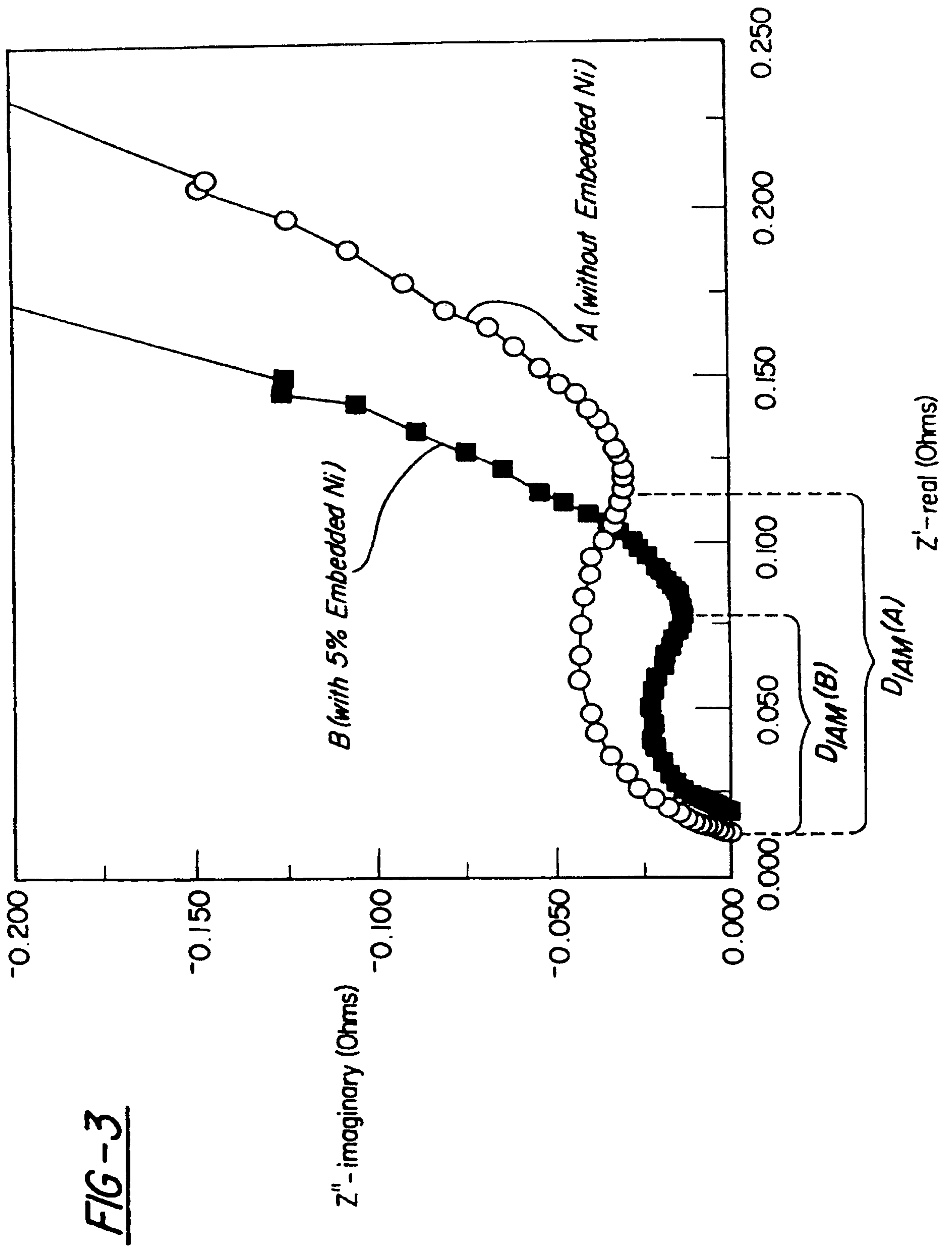


FIG - 2





4/4

