

COMPOSITE POSITIVE ELECTRODE MATERIAL
AND METHOD FOR MAKING SAME

FIELD OF THE INVENTION

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.

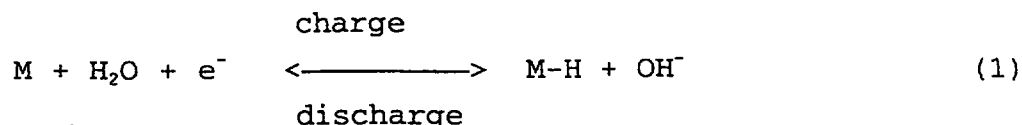
BACKGROUND OF THE INVENTION

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.

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.

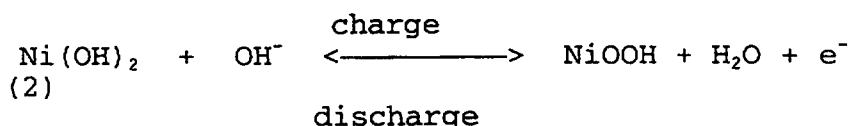
Ni-MH cells utilize a negative electrode that is capable of the reversible electrochemical storage of hydrogen. Ni-MH cells usually employ a positive electrode of nickel hydroxide material. The negative and positive electrodes are spaced apart in the alkaline electrolyte. Upon application of an electrical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

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.

In alkaline rechargeable cells, the discharge capacity of
20 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
25 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.

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.

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 β II phase to a β 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 β II and β III

0 limitations and cycling between a highly oxidized γ -phase
nickel hydroxide phase and the β 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 γ -phase, even though the higher attainable capacity
through the use of γ -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
 γ -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 γ -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 γ -NiOOH in
10 the nickel electrode is caused
by the large change of the
density from high density β -
NiOOH to low density γ -NiOOH.
The inventors have already
15 found that the production of γ -
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

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
oxygen overvoltage during charging. The further external
20 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

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,

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 γ -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

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 β II- β III phase nickel hydroxide and α - γ or β II- γ 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 γ -phase state). However, by suppressing or at
least significantly inhibiting γ -phase formation, the nickel
20 hydroxide is limited to transferring no more than one electron
per Ni atom. Further, in order to effectively inhibit γ -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.

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

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

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

5 The second way in which artisans have increased the
conductivity of nickel hydroxide is by co-precipitating cobalt
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

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

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
and without embedded nickel particles; and

15 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
and methods for making the improved materials. Disclosed
25 herein is a composite positive electrode material for use in
electrochemical cells. Generally, the composite positive

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

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

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^3 , and a BET of about 1.75
15 m^2/g .

The conductive material may take the form of a conductive
5 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.

While not wishing to be bound by theory, the inventors
15 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.

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)_2) 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

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

The protonic conductivity (i.e., the conductivity of
protons) in a typical nickel hydroxide particle is dominated
5 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

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

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,
parallelepiped, 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

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

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

The nickel hydroxide material may comprise a
compositionally and structurally disordered multiphase nickel
5 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
10 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
15 commonly assigned U.S. Patent No. 5,637,423 the contents of
which is incorporated by reference herein.

The nickel hydroxide materials may be multiphase
polycrystalline materials having at least one gamma-phase that
contain compositional modifiers or combinations of
20 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, LaH₃, Mg, Mn,
Ru, Sb, Sn, TiH₂, 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

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.

Preferably, one of the chemical modifiers is chosen from
the group consisting of Al, Ba, Ca, Co, Cr, Cu, F, Fe, K, Li,
25 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

0 alloy. Preferably, the compositional modifiers are chosen
from the group consisting of Al, Bi, Co, Cr, Cu, Fe, In, LaH₃,
Mn, Ru, Sb, Sn, TiH₂, 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, LaH₃, Mn, Ru, Sb,
5 Sn, TiH₂, 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

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.

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

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

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.

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 CoSO_4 , 15.5 grams MgSO_4 , and 11.2 grams of ZnSO_4 to 0.058
gallons of water and 1.25 gallons of 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

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.

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

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

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

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

Table

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

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 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 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 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

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



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 AND COMPRISES
10 A METAL.

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

4. The composite positive electrode material of claim 1,
15 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.

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- 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.

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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.

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

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

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

20 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
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.

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

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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⁺ oxidation state and a 3.5⁺, 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.

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- 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, LaH₃,
Mn, Ru, Sb, Sn, TiH₂, 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, LaH₃, Mn, Ru, Sb, Sn, TiH₂, 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, LaH₃,
Mn, Ru, Sb, Sn, TiH₂, 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;



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,



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.



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



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



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,
10 wherein said nucleating particle determines the average shape
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:

20 combining a metal ion solution, a caustic solution, and
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:



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