Surface Modification to Improve Hydrogen Entry Efficiency and Storage Capabilities of Metal Hydride Alloys
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**Objectives:** To develop anode materials for Ni-MH cells with high capacity and constant cycle life

**Approach:** (1) Recognize the importance of particle pulverization and corrosion processes in developing high cycle life alloys. (2) Modify the hydriding and dehydriding kinetics at the surface by electroless coatings. (3) Use EIS to understand the alloy oxidation during cycling.

**Accomplishments:** (1) Developed an in-situ technique to calculate particle size and evaluate pulverization in MH alloys during cycling. (2) Established a methodology for determination of thermodynamic, transport and kinetic parameters of hydride alloys. (3) Developed superior electrodes with high capacity, long cycle life and good energy density by various electroless coatings.

**Impact & Transition:** (1) Would lead to the development of high stability, low Co content alloys. (2) Modifying electrode kinetics would lead to the development of Magnesium based A₂B hydrides.

![Metal Hydride Test Station (top) and alloy oxidation in bare metal hydrides (bottom)](image)
**Ni-MH Battery**

**At Ni Electrode**

$$\text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \quad \leftrightarrow \quad \text{Ni(OH)}_2 + \text{OH}^-$$

**At MH Electrode**

$$\text{MH} + \text{OH}^- \quad \leftrightarrow \quad \text{M} + \text{H}_2\text{O} + \text{e}^-$$

**Cell Reaction**

$$\text{NiOOH} + \text{MH} \quad \leftrightarrow \quad \text{Ni(OH)}_2 + \text{M}$$

**Overcharge Reactions**

$$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \ (0.401 \text{ V})$$

$$\text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^- \ (-0.828 \text{ V})$$

Loss in cycle life due to metal hydride electrode
Motivation

- To study various coatings in improving the performance of metal hydride alloys
- To develop an optimized coating for high alloy capacity and long cycle life through electrochemical and material characterization
Problem Definition

- Capacity decreases during cycling.
- Causes for capacity decay
  - Particle pulverization due to volume expansion/contraction during hydrogen intercalation.
  - Alloy oxidation to inactive material and poor contact of the oxidized alloy.
Alloy Pulverization

SEM of Hydride Alloy After 30 and 650 Cycles in Toshiba Cells
Corrosion Mechanism in LaNi$_{5-x}$Sn$_x$ Alloy

LaNi$_{5-x}$M$_x$ + 3H$_2$O $\rightarrow$ La(OH)$_3$ + Ni$_{5-x}$M$_x$ + 3/2 H$_2$

LaNi$_{5-x}$M$_x$ + 3OH$^-$ $\rightarrow$ La(OH)$_3$ + Ni$_{5-x}$M$_x$ + 3e$^-$

3H$_2$O + 3e$^- \leftrightarrow$ 3OH$^-$ + 3/2H$_2$

EPMA analysis showing lanthanum oxidation during cycling

Segregation of Hydride Alloys

La diffuses to the surface of the alloy and is oxidized
Capacity Decay for LaNi$_{4.27}$Sn$_{0.24}$ Alloy
Conventional Approach To Solve Capacity Fade

Philips-Hughes Aircraft Co. and BNL tried with partial substitutions in the alloy to stabilize the electrode thermodynamics

Limitations

- Does not eliminate the problem of alloy corrosion during cycling.
- Does not prevent the surface oxidation and subsequent segregation of active material.
- Substitutions decrease the capacity of the alloy.
Our Approach

- Understand the alloy pulverization and optimize the particle size to reduce pulverization.
- Recognize the importance of corrosion processes in developing high cycle life alloys.
- Prevent the oxidation of the alloy during cycling.
- Eliminate any shedding of pulverized active material.
- Modify the kinetics of the hydriding/dehydriding reaction at the surface.
Objectives

- Develop novel techniques for electrochemical characterization of metal hydride alloys.
- Develop a technique for synthesizing AB$_5$ type hydrides loaded with nano-sized catalytic particles of Cu, Pd, Ni, Co.
- Study the electrocatalytic ability and cycling performance of these novel materials.
- Optimize the loading of catalyst on the surface of hydrides.
Plan of Study

Alloys Studied
LaNi$_{4.27}$Sn$_{0.24}$
LaNi$_{4.25}$Al$_{0.75}$
LaNi$_{4.5}$Al$_{0.5}$
La$_{0.65}$Ce$_{0.35}$Ni$_{3.55}$Co$_{0.75}$Mn$_{0.4}$Al$_{0.3}$

Encapsulation with Nanosized Amorphous Cu, Pd, Ni, Co Particles

Material Characterization
SEM, TEM Analysis
BET Analysis
EPMA, EDAX, XRD

Electrochemical Characterization
Cycling studies
AC Impedance
Cyclic Voltammetry,
Linear Polarization
Impedance Model for Determination of Diffusion Coefficient and Particle Size

\[ MH_{x,\text{ads}} + x\text{OH}^- \leftrightarrow M + x\text{H}_2\text{O} + xe^- \]

Assuming Fickian diffusion and solving for the concentration of hydrogen in the particle

\[
\bar{c}_s = \frac{c^0}{p} - \frac{j\omega_{MH}R_{\text{MH}}}{a_{\text{MH}}V(1-\varepsilon)FD}\left(\frac{pR^2}{D}\right)^{\frac{\sinh\left(\sqrt{\frac{pR^2}{D}}\right)}{\cosh\left(\sqrt{\frac{pR^2}{D}}\right)-\sinh\left(\sqrt{\frac{pR^2}{D}}\right)}}
\]

Faradaic Impedance is given by

\[ Z = \frac{d\eta}{dj} \]
Impedance at the interface

\[ Z(\omega) = \frac{\partial \bar{\eta}_s}{\partial j} + \frac{(1-i)\sigma}{\sqrt{\omega \left[ \coth[(1+i)\psi] - \frac{1-i}{2\psi} \right]}} \]

\[ \sigma = \left( \frac{\partial j/\partial c_s}{\partial j/\partial \bar{\eta}_s} \right) \left[ \frac{w_{MH}}{a_{MH} V(1-\varepsilon)F\sqrt{2D}} \right] \]

\[ Z(\omega) = \text{Re} + i \text{Im} \]

\[ \text{Im} = -\frac{\sigma}{\sqrt{\omega}} \left[ \frac{(T_1 + T_2)}{(T_1^2 + T_2^2)} \right] \quad \text{Re} = \frac{\sigma}{\sqrt{\omega}} \left[ \frac{(T_1 - T_2)}{(T_1^2 + T_2^2)} \right] \]

\[ \psi = \sqrt{\frac{\omega R^2}{2D}} \]
Increasing the diffusion coefficient reduces the time for diffusion.

Hence the transition appears at high frequencies.

Particle size in contrast to diffusion coefficient leads to larger diffusion times.

Hence transition shifts to lower frequencies.
Particle Size Determination using EIS

Impedance response of cobalt coated alloy characterized by semi-infinite, transition and finite diffusion regimes

Exponential fit of Nyquist transition regime

Particle Size = 32 µm

Imp = 0.1018 * e^{(0.4609*Re)}
Determination of hydrogen diffusion coefficient

Governing Equation:
\[
\frac{\partial (rc)}{\partial t} = D \frac{\partial^2 (rc)}{\partial r^2}
\]

Analytical Solution:
\[
\frac{c - c_o}{c_s - c_o} = 1 + \frac{2a}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n \pi r}{n a} e^{-\frac{D n^2 \pi^2 t}{a^2}}
\]

Constant surface concentration:
\[
\log i = \log \left[ \pm \frac{6FD}{da^2} (c_o - c_s) \right] - \frac{\pi^2 D}{2.303 a^2 t}
\]

Constant flux at the surface:
\[
\frac{D}{a^2} = \frac{1}{15 \left( \frac{Q_o}{i} - \tau \right)}; \quad Q_1 = Q_o - \tau i = \pm \frac{i a^2}{15 D}
\]

Hydrogen Diffusion Coefficient Determination

\[
\frac{D}{a^2} = \frac{1}{15\left(\frac{Q_o}{i} - \tau\right)} = 4 \times 10^{-5} \text{ s}^{-1}
\]
Particle Size Determination using EIS

Impedance response of cobalt coated alloy characterized by semi-infinite, transition and finite diffusion regimes.

Exponential fit of Nyquist transition regime

Particle Size = 32 µm
Measurement of Electrochemical Kinetic Parameters

Tafel:
\[ \eta = \frac{2.3\,RT}{\alpha\,n\,F} \log i_o - \frac{2.3\,RT}{\alpha\,n\,F} \log i_c ; \eta = \frac{RT}{F} \ln \frac{i}{i_o} \]

Microcurrent current density:
\[ i' = i_o' \left\{ \frac{C_{OH^-}(p)}{C_{OH^-}(b)} e^{\frac{(1-\beta)F}{RT} \eta} - \frac{C_{H_2O}(p)}{C_{H_2O}(b)} e^{-\frac{\beta F}{RT} \eta} \right\} \]

\[ i = i_o \left\{ \frac{C_{OH^-}(i)}{C_{OH^-}(b)} e^{-\frac{(1-\beta)F}{RT} \eta_i} \log \frac{\sqrt{K}}{\sqrt{K}} - \frac{C_{H_2O}(i)}{C_{H_2O}(b)} e^{-\frac{\beta F}{RT} \eta_i} \right\} \]

\[ K = \frac{i_o LM}{A s FD_{H_2O}} \left[ e^{\frac{\beta F}{RT} \eta_i} + e^{-\frac{(1-\beta)F}{RT} \eta_i} \right] \]

Determination of Exchange Current Density

\[ i = i_o \left\{ e^{\frac{(1-\beta)F}{RT} \eta_i} - e^{\frac{-\beta F}{RT} \eta_i} \right\} \]

\[ i = \frac{i_o F}{RT} \eta \]

\[ R_p = \frac{RT}{F \, i_o} \]

Electrode Thermodynamics

\[ M + xH_2O + xe^- \underset{\text{charge}}{\iff} \underset{\text{discharge}}{\text{MH}_{x,ads} + xOH^-} \]

Electrode potential:

\[ \Phi_{eq} = \Phi^o - \frac{RT}{F} \ln \frac{\hat{a}_H}{\hat{a}_M} \]

\[ M = \text{Free Metal Sites} \]

Thermodynamic model for excess energy:

\[ G_E = RT\left[ (1 - \hat{c}_s) \ln \gamma_M + \hat{c}_s \ln \gamma_H \right] \]

\[ \ln \gamma_H = \frac{A}{RT} \left( 1 - \hat{c}_s \right)^2 \]

\[ \ln \gamma_M = \frac{A}{RT} \hat{c}_s^2 \]

Electrode potential considering nonidealities in \( \gamma \):

\[ \Phi_{eq} = \Phi^o - \frac{RT}{F} \ln \left( 1 - \hat{c}_s \right) + \frac{A}{F} \left[ 2 \hat{c}_s - 1 \right] \]

Change in Equilibrium Potential with SOC

**Graph**

- **Y-axis**: $\Phi_\text{eq}$ (V)
- **X-axis**: State of Charge (%)

**Data Points**
- Experimental
- Model

**Values**
- $\Phi_\text{eq}$ values range from -0.97 V to -0.88 V as the State of Charge increases from 0% to 100%.
Electrode Kinetics

Modified Butler-Volmer expression for hydride electrode:

\[
j' = j_o \left\{ \frac{\hat{c}_s^\beta}{(1 - \hat{c}_s)^\beta} - \frac{\beta F}{RT} \left[ \Phi - \Phi^o - \frac{A}{F} (2 \hat{c}_s - 1) \right] \right\} e^{-(1 - \beta)F} \left[ \Phi - \Phi^o - \frac{A}{F} (2 \hat{c}_s - 1) \right] \frac{e^{-\beta}}{(1 - \hat{c}_s)^{(1 - \beta)}}
\]

Concentration dependent exchange current density:

\[
 j_o = j_{o,ref} \hat{c}_s^{p(1 - \beta)}(1 - \hat{c}_s)^{q\beta} e^{\frac{A}{RT} [p(1 - \hat{c}_s)^2 (1 - \beta) + q \beta \hat{c}_s^2]}
\]

\[
 j_{o,ref} = \frac{j_{o,50\% SOC}}{0.5^{p + \beta(q - p)} e^{\frac{0.5^2 A}{RT} [p + \beta(q - p)]}}
\]
Change in Exchange Current Density With State of Charge

![Graph showing the change in exchange current density with state of charge. The graph has a logarithmic scale on the y-axis and a linear scale on the x-axis. The x-axis represents the state of charge (%) ranging from 0 to 100, while the y-axis represents the current density, $j_0$, in mA/g ranging from $10^0$ to $10^1$. The graph includes experimental data points and a model fit represented by a dashed line.]
Microencapsulation
Surface treatment of the alloy by electroless plating of a porous thin film of copper, nickel, palladium or cobalt

Why Microencapsulation?

Microencapsulation of the alloy particles will:

- act as a barrier film for protecting the alloy surface from oxygen
- facilitate the charge transfer reaction on the alloy surface thereby improving the electrocatalytic activity
- increase the electrical and thermal conductivity of the alloy
- prevent shedding of active material from the electrode and hence reduce the effect of pulverization
Copper Microencapsulation

- Developed a deposition technique for coating AB$_5$ hydrides with Cu.
- Determined the electrochemical parameters for Cu coated LaNi$_{4.27}$Sn$_{0.24}$ alloys
  - Symmetry Factor = 0.53
  - Theoretical Capacity = 275 mAh/g
  - D/a$^2$ = 3.1 X 10$^{-5}$ s$^{-1}$
  - Exchange current density = 24 mA/g (15% above bare alloy)
- Cu coating acts as a microcurrent collector and facilitates the charge transfer on the surface of the particle.

Palladium Microencapsulation

- Synthesized Pd loaded LaNi$_{4.25}$Al$_{0.75}$ with different amounts of Pd on surface
- Studied the various resistances for Pd coated LaNi$_{4.25}$Al$_{0.75}$ electrode using electrochemical impedance spectroscopy
- Determined the electrochemical parameters for Pd coated LaNi$_{4.25}$Sn$_{0.75}$ alloys
  - Hydrogen reaction order = 0.2
  - Theoretical Capacity = 295 mAh/g
  - Symmetry factor = 0.53
  - Exchange current density = 70 mA/g
- Pd coating increases the capacity of the metal hydride alloy. (295 mAh/g compared to 122 mAh/g)

Nickel Microencapsulation

Overall Reaction

\[ \text{Ni}^{2+} + 2\text{H}_2\text{PO}_2^- + 2\text{H}_2\text{O} \rightarrow \text{Ni} + 2\text{H}^+ + 2\text{H}_2\text{PO}_3^- + \text{H}_2 \]

Catalytic Decomposition of Hypophosphite Ion

\[ \text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \xrightarrow{\text{Catalytic surface}} 2\text{H}^+ + \text{H}_2\text{PO}_3^- + 2\text{e}^- \]

Ni Deposition

\[ \text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni} \]

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]

Deposition of Phosphorus

\[ \text{H}_2\text{PO}_2^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{P} + 2\text{H}_2\text{O} \]
After 3 minutes

After 6 minutes

After 13 minutes
TEM and SEM analysis after complete Ni plating
Novel Electroless Deposition Process

- One-step process
- Does not involve expensive SnCl₂ and PdCl₂
- Electroless coating involving no external current
- Activation and deposition are done in a single bath
<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-38 µm</td>
<td>0.1170</td>
<td>2.5919</td>
</tr>
<tr>
<td>63-90 µm</td>
<td>0.0342</td>
<td>2.3044</td>
</tr>
<tr>
<td>90-106 µm</td>
<td>0.0250</td>
<td>1.3165</td>
</tr>
<tr>
<td>150-180 µm</td>
<td>0.0140</td>
<td>0.4467</td>
</tr>
<tr>
<td>&gt; 250 µm</td>
<td>0.0136</td>
<td>0.4571</td>
</tr>
</tbody>
</table>
Co Microencapsulation
Experimental

• Pellet electrode was prepared from cobalt plated LaNi$_{4.27}$Sn$_{0.24}$ alloy

• Cycling and characterization studies were done in a 3 electrode setup with Ni counter electrode and Hg/HgO reference electrode

• Electrode was activated with 10 charge-discharge cycles

**Charge-discharge Studies**

Objective: to determine the dependence of exchange current density, equilibrium potential on the SOC

- charge the electrode under a constant current mode until the hydrogen content reaches its saturated value
- perform polarization studies after the electrode has stabilized
- discharge the electrode at a constant current for a specific period of time to reach the desired SOC
- repeat the studies until the electrode is discharged to a potential of -0.6 V
Charge-Discharge Characteristics of Bare and Cobalt Coated LaNi$_{4.27}$Sn$_{0.24}$
Discharge Characteristics of Cobalt Coated \( \text{LaNi}_{4.27}\text{Sn}_{0.24} \) at different Charging Times
Effect of Nanosized Co-P on Discharge Capacity

- Hydrogen Absorption/Desorption

\[
\text{MH}_{x,\text{ads}} + x\text{OH}^- \leftrightarrow M + x\text{H}_2\text{O} + xe^- \\
E = -930 \text{ mV vs. } \text{Hg/HgO} \quad [1]
\]

- Cobalt Faradaic Reaction

\[
\text{Oxdn} \quad \text{Rdn} \\
\text{Co} + 2\text{OH}^- \leftrightarrow \text{Co(OH)}_2 + 2e^- \\
E = -800 \text{ mV vs. } \text{Hg/HgO} \quad [2]
\]
Discharge Characteristics of Pure Cobalt and Cobalt Coated LaNi$_{4.27}$Sn$_{0.24}$ Electrodes
# Cobalt Utilization Studies

<table>
<thead>
<tr>
<th>Charge time (hours)</th>
<th>Total discharge capacity (mAh/g)</th>
<th>Discharge capacity due to hydride (mAh/g)</th>
<th>Discharge capacity due to cobalt (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>336</td>
<td>175.05</td>
<td>160.95</td>
</tr>
<tr>
<td>7.5</td>
<td>261.00</td>
<td>135.59</td>
<td>125.41</td>
</tr>
<tr>
<td>5</td>
<td>161.92</td>
<td>69.20</td>
<td>92.72</td>
</tr>
<tr>
<td>3</td>
<td>107.63</td>
<td>30.54</td>
<td>77.09</td>
</tr>
<tr>
<td>2</td>
<td>62.56</td>
<td>7.91</td>
<td>54.65</td>
</tr>
</tbody>
</table>
CV’s before Activation
CV’s after Activation

Potential (V vs Hg/HgO)

Current (mA/g)

-200 -100 0 100 200

-1.0 -0.9 -0.8 -0.7 -0.6

cobalt coated

cobalt mixed
Cycle Life Studies

- Co encapsulated, Thickness = 0.789 µm
- Co encapsulated, Thickness = 0.345 µm
- Co Mixed
- Bare

Capacity (mAh/g) vs Number of cycles
Cobalt Utilization Studies

<table>
<thead>
<tr>
<th>Coating thickness (µm)</th>
<th>Capacity due to cobalt (mAh/g)</th>
<th>Cobalt utilization (%)</th>
<th>Cycle life</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.285</td>
<td>710</td>
<td>78.89</td>
<td>40</td>
</tr>
<tr>
<td>0.338</td>
<td>640</td>
<td>71.11</td>
<td>60</td>
</tr>
<tr>
<td>0.345</td>
<td>600</td>
<td>66.67</td>
<td>90</td>
</tr>
<tr>
<td>0.789</td>
<td>580</td>
<td>64.44</td>
<td>200+</td>
</tr>
</tbody>
</table>

Cobalt utilization = \( \frac{\text{Capacity due to cobalt}}{\text{Theoretical Co capacity (900 mAh/g)}} \times 100\%

Change in Exchange Current Density of $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ Alloy Before and After Coating
Change in Equilibrium Potential of Ni and Co Coated Alloy

-0.95  -0.93  -0.91  -0.89  -0.87  -0.85  -0.83  -0.81  -0.79  -0.77  -0.75  -0.73
Potential (mV)

Nickel plated
Bare alloy
Cobalt plated
Ni-Co plated

SOC (%)
Cycling of Co coated \( \text{LaNi}_{4.27}\text{Sn}_{0.24} \) alloy in 6 M KOH.
Electron Probe Microscopic Analysis on Cobalt Encapsulated Alloy

EPMA for Nickel (left) and Lanthanum (right). Nickel and Lanthanum are deficient on the surface.

EPMA for Cobalt (left) and Oxygen (right). Cobalt is uniformly coated over the surface and is present as Co(OH)$_2$. 

80 µm
Pulverization in Bare and Cobalt Coated $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ electrodes with cycling
Conclusions

- Potentiostatic and galvanostatic technique has been developed for determination of the diffusion coefficient of hydrogen through MH electrodes.
- Transport and electrochemical kinetic parameters of bare and Cu/Pd coated alloys were determined using porous electrode theory.
- Cu and Pd coatings increase the electrocatalytic activity for hydrogen entry into the alloy.
- Developed a theoretical model to study the performance of the hydride electrode.
- Studied the change in electrode parameters as a function of SOC.
Conclusions

- Developed a novel one-step plating process for microencapsulation of hydride alloys
- Deposited Co coatings on the surface of LaNi$_{4.27}$Sn$_{0.24}$ alloy using the novel deposition technique
- Studied the unique behavior of these coatings in alkaline solutions
- Developed superior electrodes with constant capacity and longer cycle life using Co-P nanostructures
- A ten-fold increase in cycle life and a 25% increase in capacity have been achieved using these coatings
Other Accomplishments

- Effect of temperature on performance of MH electrodes has been determined.
- The electrode capacity and utilization were determined for different electrode weights and binder contents.
- Did electrochemical and material characterization on Ni-Co-P and Co-Ni-P coated LaNi$_{4.27}$Sn$_{0.24}$ alloys
- Determined the hydrogen diffusion coefficient in hydride alloys using impedance spectroscopy
Future Directions

- Synthesize surface modified AB\(_5\) and AB\(_2\) alloys
- Synthesis of nanocrystalline alloy electrodes through ball milling.
- Propose to synthesize A\(_2\)B alloys - Mg doped with Ni, Co, Ti, Zr alloys.
- Form a Ni-rich surface layer and increase surface area, improve reactivity and corrosion resistance
Acknowledgments

Financial support by the Exploratory Technology Research (ETR) Program, which is supported by the Office of Transportation Technologies (OTT) of the US Department of Energy (DOE), Subcontract No. 4614610 is acknowledged gratefully.