UNIVERSITÉ PARIS-EST

ÉCOLE DOCTORALE UNIVERSITÉ PARIS-EST
Sciences, Ingénierie et Environnement

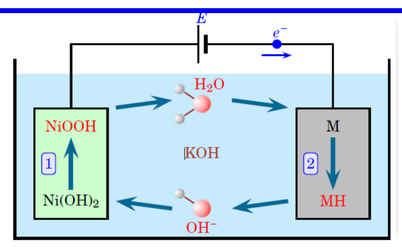
Hydrogen absorption properties and alkaline corrosion of $Y_{2-x}Mg_xNi_7$ for future application as negative electrodes in Ni-MH battery

N. Madern, V. Charbonnier, J. Monnier, J. Zhang, M. Latroche

Université Paris-Est, Institut de Chimie et des Matériaux Paris-Est, UMR 7182 CNRS - UPEC, 2, rue Henri Dunant, 94320 Thiais, France

Introduction

Better capacity and cycle life are generally the main goal of the research in the Ni-*M*H batteries field. In these batteries, the cycle life may be limited by corrosion.



Schematic drawing of a Ni-*M*H accumulator

Goal

The **goal of this thesis** is to study the influence of various substitutions in A_2B_7 structures for future use as Ni-*M*H negative electrode materials.
This poster presents the influence of Mg substitution on the corrosion and H sorption properties of Y_2Ni_7–type material.

Context

H sorption

Electrochemical reaction:

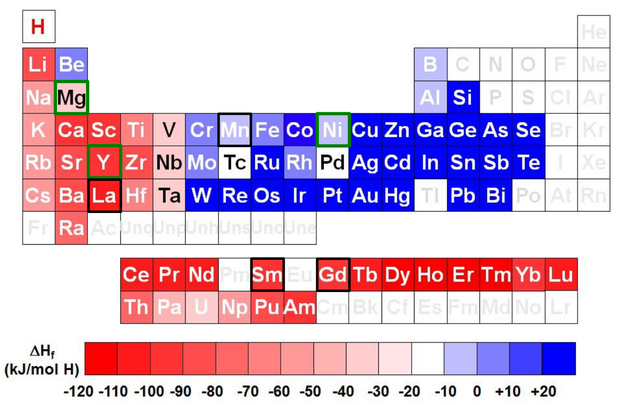
$M + x\ H_2O + x\ e^- \leftrightarrow MH_x + x\ OH^-$

linked with

Solid-Gas reaction:

$M + \frac{x}{2} H_2 \leftrightarrow MH_x$

Which elements absorb hydrogen ?

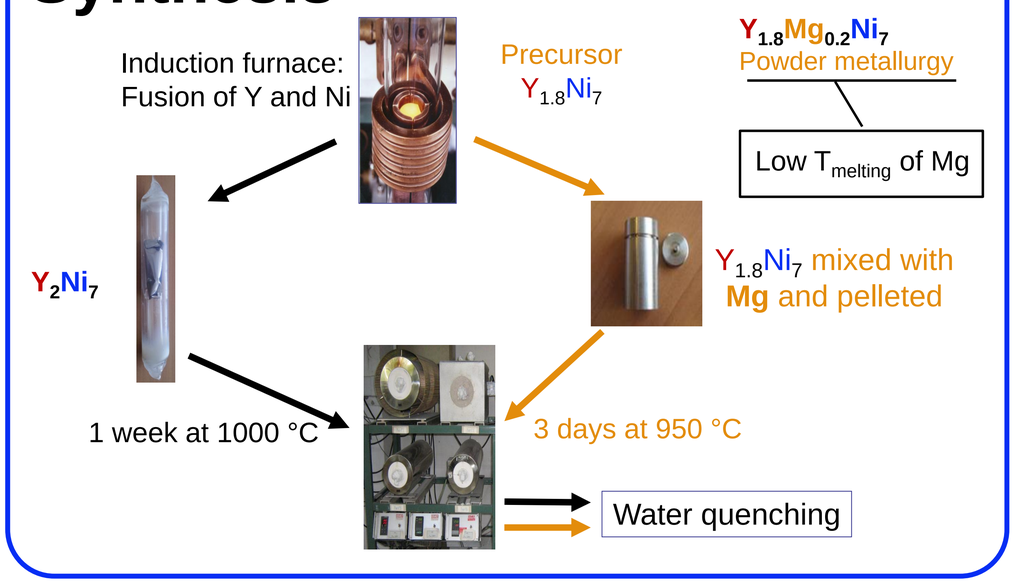


AH_y: stable hydride forms at low pressure

BH_z: unstable hydride forms at high pressure

- Alloys AB_x allow to tune the equilibrium pressure
- Light elements Y and Mg [1] are chosen with Ni

Synthesis

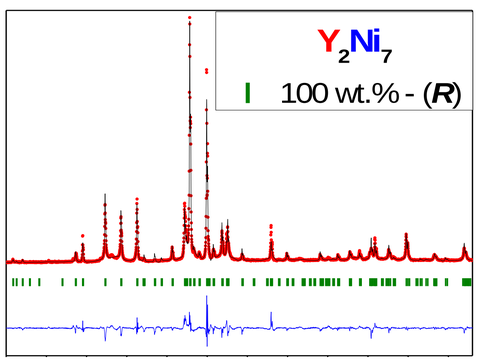


Structural characterization: XRD

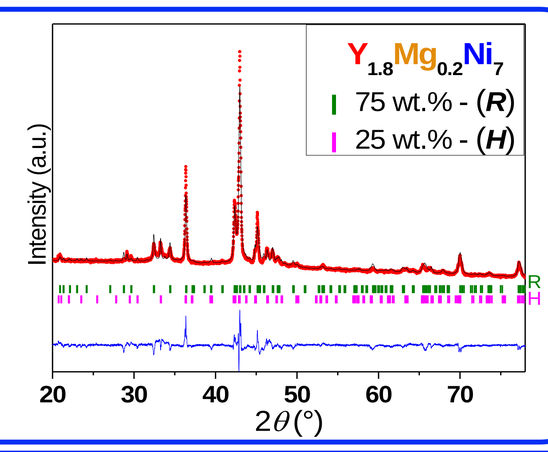
Composition of both alloys confirmed by EPMA

Structure
$A_2B_7 \leftrightarrow A_4B_{14}$

A_2B_4 + 2 x AB_5



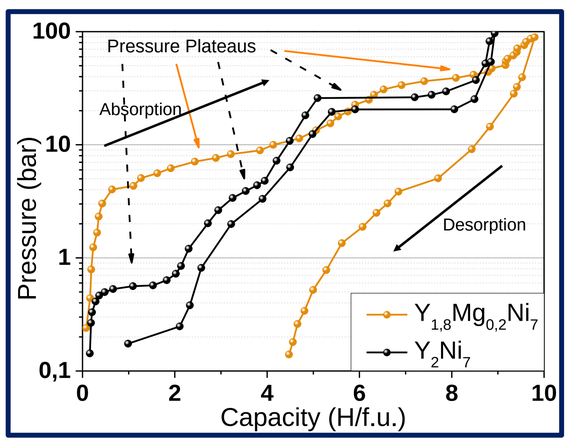
Y_2Ni_4 → A_2B_7 (*R*) + $Y_{1,6}Mg_{0,4}Ni_4$ → A_2B_7 (*H*)



Mg influence on H sorption

Y_2Ni_7:

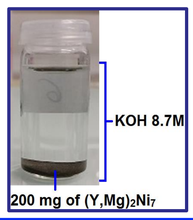
- High Δ*P* between 1st and last plateaus
- Good reversibility



$Y_{1.8}Mg_{0.2}Ni_7$:

- Lower Δ*P* between plateaus
- High hysteresis
- Mg ↘ the lattice parameters of A_2B_4 thus ↗ P_{eq1}
  - Mg increases the capacity and lightens the alloy
    → Capacity increases from 1.53 to **1.71** wt.%
  - $Y_{1.6}Mg_{0.4}Ni_4$ should be more stable than Y_2Ni_4
    → better reversibility is expected
  - High hysteresis of $Y_{1.8}Mg_{0.2}Ni_7$: bad reversibility ? Kinetics ?

Mg influence on the corrosion



Corrosion experiments

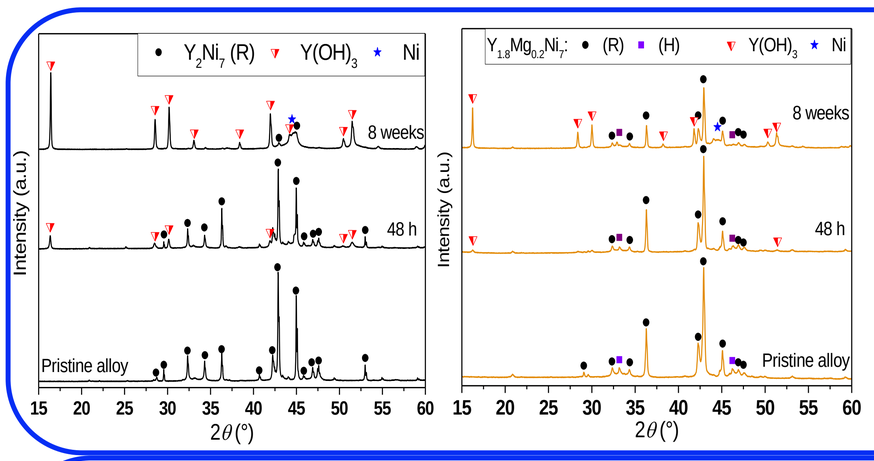
- Samples soaked
- Rinced and dried

Mass gain

Corrosion reaction:

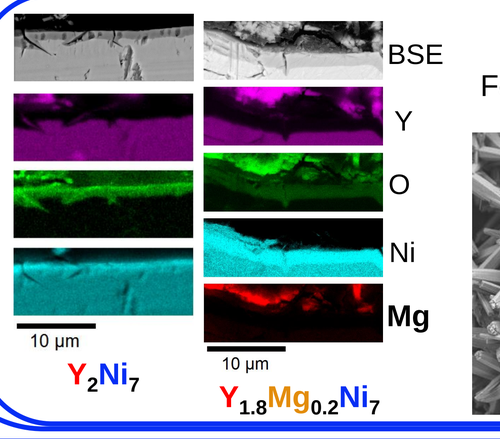
$Y_2Ni_7 + 6\ H_2O \rightarrow 2\ Y(OH)_3 + 7\ Ni + 3\ H_2$

At 18 weeks:
Y_2Ni_7 : Δm = 9.7 %
$Y_{1.8}Mg_{0.2}Ni_7$: Δm = 6.1 %



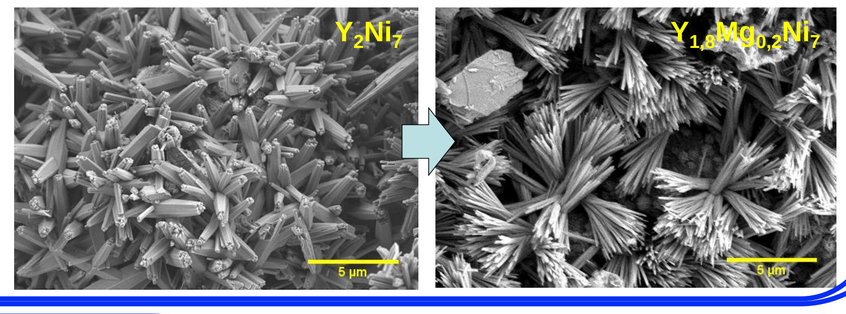
XRD

- $Y(OH)_3$ and Ni for both alloys
- No Mg related phase detected
- $Y_{1.8}Mg_{0.2}Ni_7$ corrodes slower



SEM-EDS of corroded samples

For Mg substituted { A Mg-rich layer at the top of the Ni layer; Different hydroxide needle shapes



Conclusion

\+
- Synthesis: 100% A_2Ni_7
- **Mg effects:**
  - ➢ hydrogen sorption capacity ↗
  - ➢ number of plateaus ↘
  - ➢ slower corrosion and a Mg-rich layer is observed

\-
- ➢ pressure plateaus ↗
- ➢ H sorption reversibility ↘

Perspectives

- TEM study on the Mg layer
- Continue PCT cycling
- Substitution to ↘ the pressure plateau and to ↗ hydrogen sorption reversibility

References

[1] T. Kohno, H. Yoshida, F. Kawashima, T. Inaba, I. Sakai, M. Yamamoto, M. Kanda, *Journal of alloys and compounds* **311** (2000) L5-L7
[2] V. Charbonnier, J. Zhang, J. Monnier, L. Goubault, P. Bernard, C. Magén, V. Serin and M. Latroche, *J. Phys. Chem. C* **119** (2015) 12218-12225