Magnesium based alloys as advanced anodes for the Ni-Metal Hydride batteries

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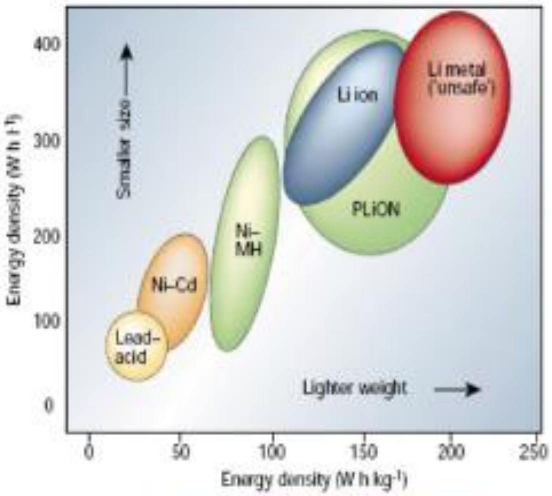
Ni-Metal Hydride Batteries

Commercial Hybrids: Exceptional Track Record of Success

- **Over 3 million hybrid cars sold with NiMH**
- **Proven safety, life time, reliability and cost**



Negative electrode

Charge

$$M + xH_2O + xe^- \Leftrightarrow MH_x + xOH^-$$

Discharge

GOALS:

HIGH VOLUMETRIC AND GRAVIMETRIC ENERGY DENSITIES

HIGH POWER DENSITY

LOW COST + HIGH CYCLE LIFE

WHY Ni METAL HYDRIDE BATTERIES?

- HIGH POWER PERFORMANCE
- LOW, SUBZERO TEMPERATURE OPERATION
- SAFETY
- LARGE BATTERY PACK SYSTEMS

Value chain for Metal Hydride batteries

SILMAG

Mg BASED METAL HYDRIDES ALLOYS FOR ANODES

NILAR

Raw material → Mg alloys → Batteries → Modules → End-user

Mg_2SiO_4

Toyota Prius

Gigacell by Kawasaki

The MOVITZ by NILAR

Mg ALLOYS

Mg: ***ABUNDANCE***
LOW DENSITY
AFFORDABLE PRICE

H STORAGE

BATTERY ELECTRODE ALLOYS

EFFECT OF MAGNESIUM ON THE STRUCTURE, THERMODYNAMICS AND KINETICS OF THE METAL-HYDROGEN INTERACTIONS

GREAT INTEREST WORLDWIDE

(Magnesium+Hydride) most publications in 1995-2013

OBJECTIVES

- High power densities
- Fast charge-discharge performance
- Low-temperature operation
- Long service life
- High safety

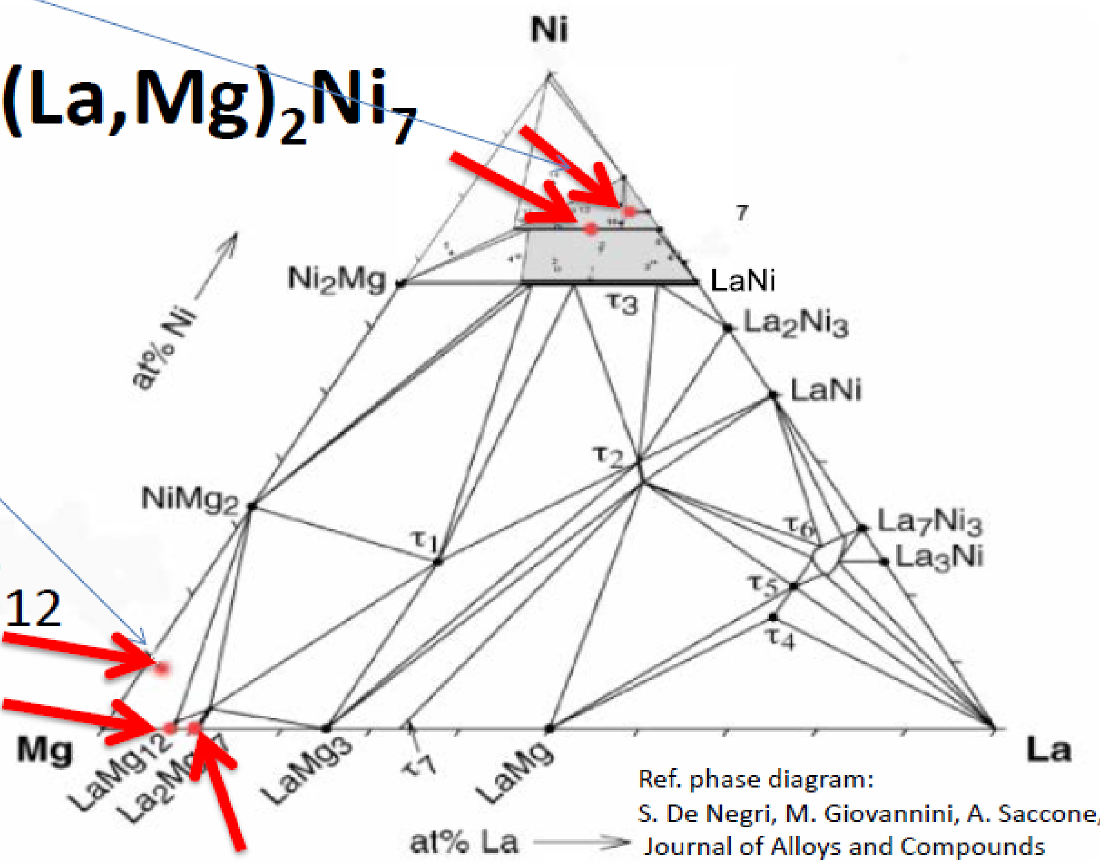
La-Mg-Ni Alloys

Ni-MH BATTERIES
La→Mg SUBSTIT.

$(La,Mg)Ni_3 + (La,Mg)_2Ni_7$

H STORAGE/
FAST H KINETICS:
Mg METAL

Eutectic
$Mg+Mg_2Ni+LaMg_{12}$
88 at% Mg



Ref. phase diagram:
S. De Negri, M. Giovannini, A. Saccone,
Journal of Alloys and Compounds
397 (2005) pp. 126-134.

$LaMg_{12}$, $LaMg_{11}Ni$, $La_2(Mg,Ni)_{17}$

INTERMETALLIC HYDRIDES: ADVANTAGES

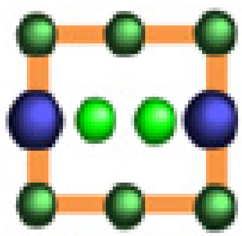
- ✓Extremely fast absorption and desorption of hydrogen gas (seconds)
- ✓Convenient operation range, below 50 ºC and at H_2 pressures (**0.1-1 bar**)
- ✓High volume density of H in the metal lattice, 1.5-2.0 times higher than for LH_2
- ✓Reversible absorption and desorption, can be repeated > 10000 times

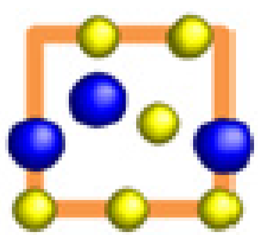
HYBRID INTERMETALLICS:

$3RM_3 = RM_5 + 2\ RM_2$

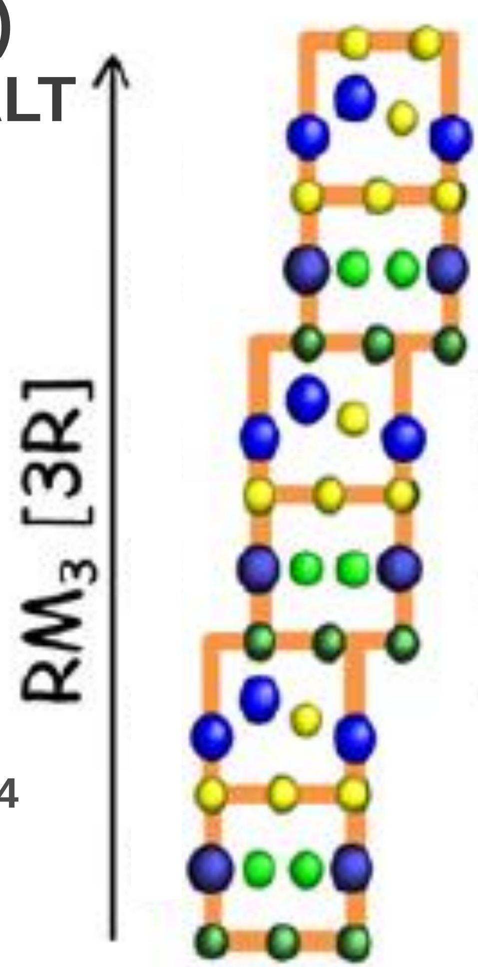
TOO UNSTABLE (P>2 bar)
NEED EXPENSIVE COBALT

$RM_5 \rightarrow RM_5H_6$





$RM_2 \rightarrow RM_2H_4$



EXCELLENT H STORAGE PERFORMANCE WHEN Mg PRESENT

RM_2 Laves type

IRREVERSIBLE H ABSORPTION-DECOMPOSITION: AMORPHISATION

RM_3 $PuNi_3$ type

FOCUS ON THE EFFECT OF MAGNESIUM

(a) Thermodynamics and phase equilibria in RE-Mg-Ni-based hydride systems

(b) Metallurgical processing of the alloys

(c) Studies of hydrogen diffusion and charge-discharge performance of the electrodes

(d) Mechanism of the processes in the metal hydride electrodes by *in situ* characterization and modelling

$(La,Pr,Nd)_{3-x}Mg_xNi_9 - H_2$ SYSTEMS

$La_{3-x}Mg_xNi_9$

$La_{3-x-y}(Pr,Nd)_yMg_xNi_9$

NANOSTRUCTURING

Rapid Solidification

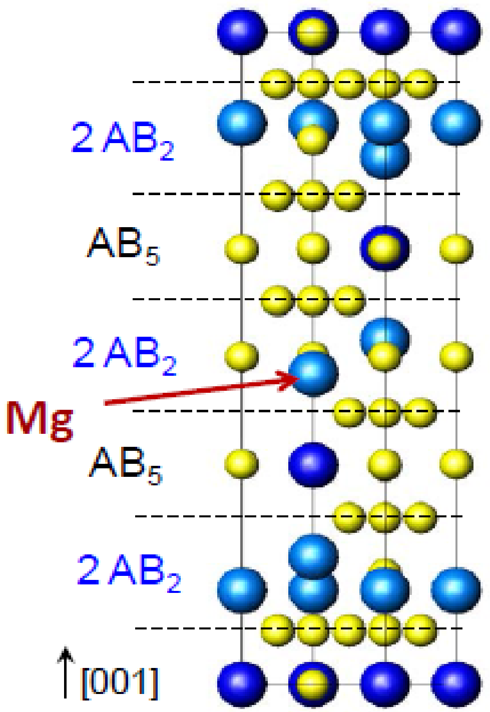
Cu wheel

Ar

HEBM
High Energy Ball Milling

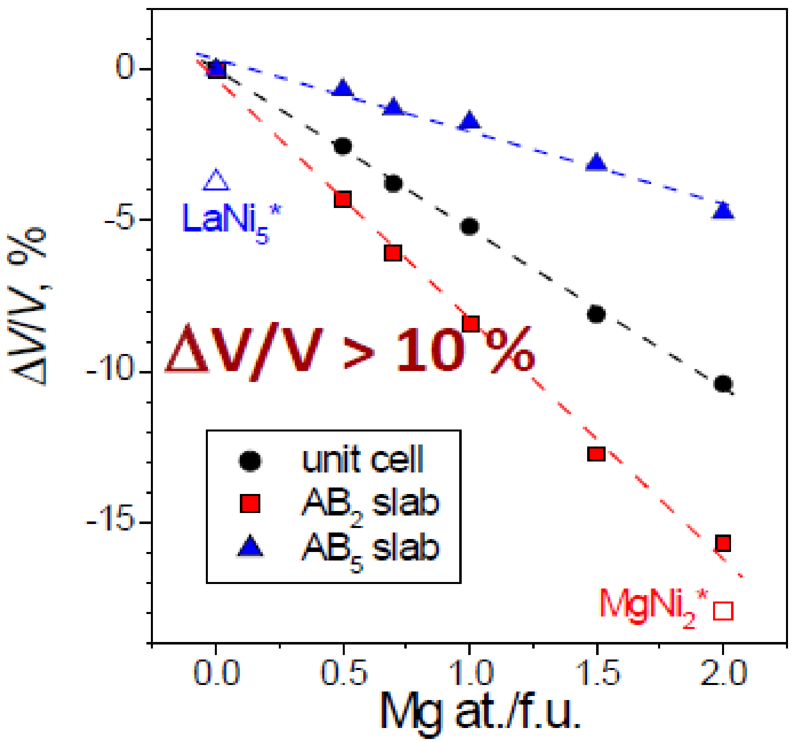
30 bar H_2

Effect of Mg ⇒ La substitution on the structure of $LaNi_3$



$r(La)$=1.87 Å
$r(Mg)$=1.60 Å

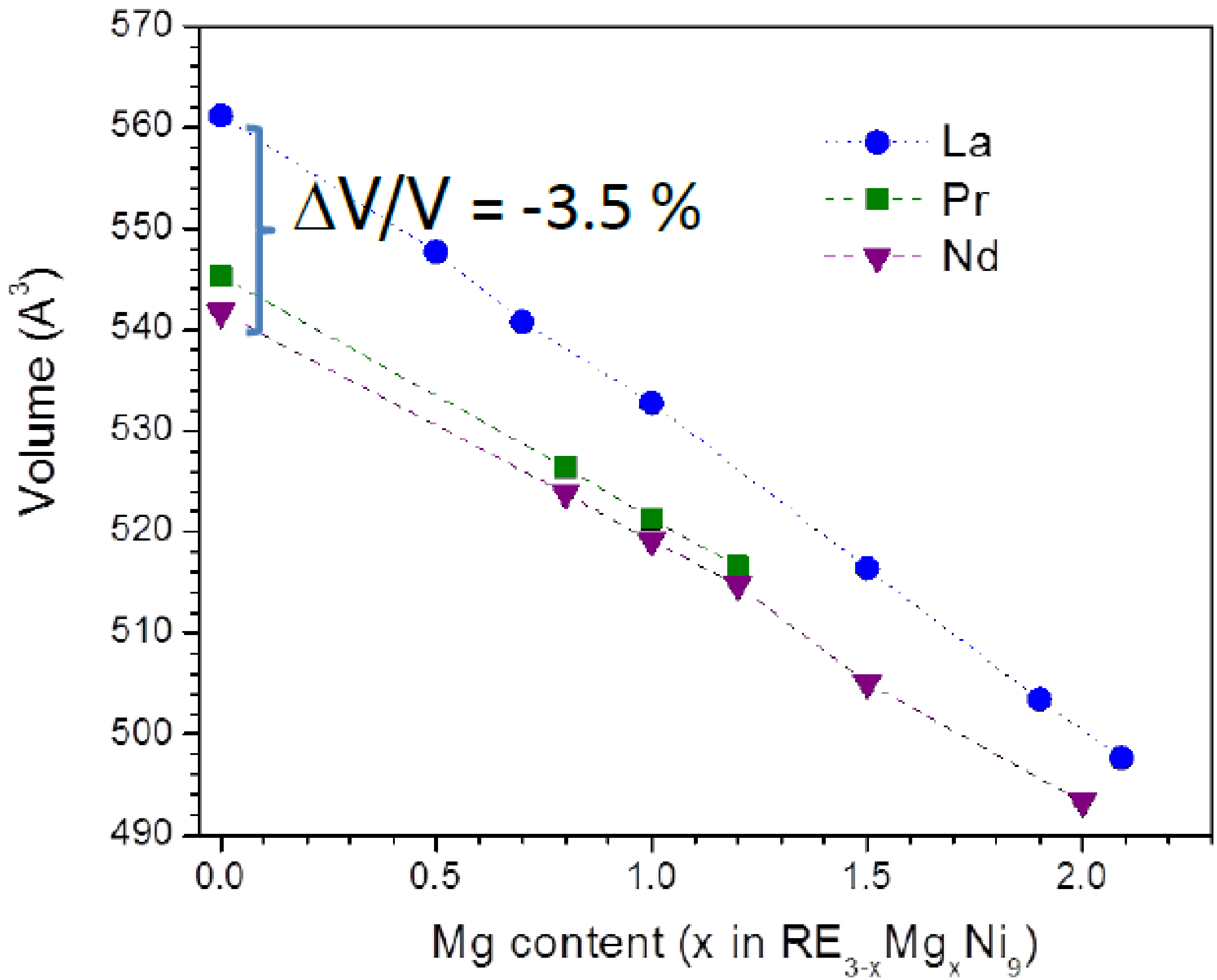
Volume of structure fragments in $La_{3-x}Mg_xNi_9$ vs. $LaNi_3$



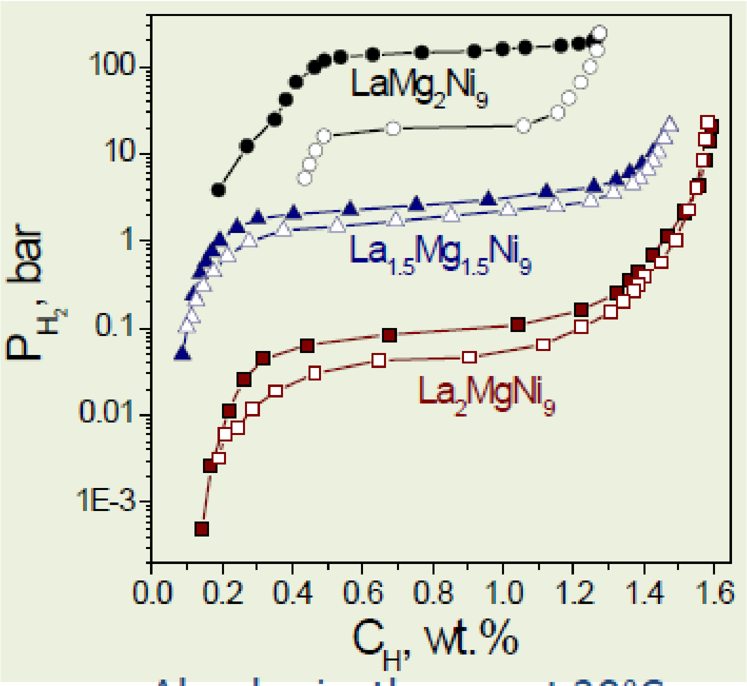
Mg substitutes La exclusively in the AB_2 layers

Significant shrinking of both AB_2 and AB_5 layers

$(La,Pr,Nd)_{3-x}Mg_xNi_9$ IMC

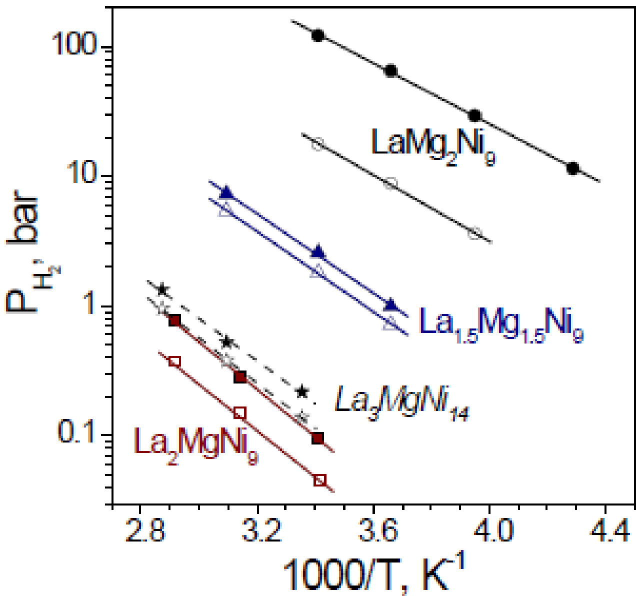


THERMODYNAMICS



Abs-des isotherms at 20°C

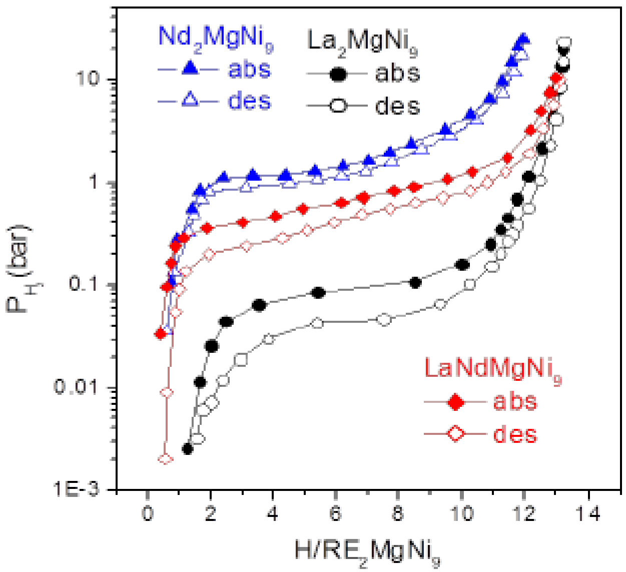
Van't Hoff plots



Dramatic change of H_2 pressures, from 0.05 to 150 bar when Mg content changes from x = 1 to x = 2

EFFECT OF SUBSTITUTION La → Pr, Nd and La → Mg

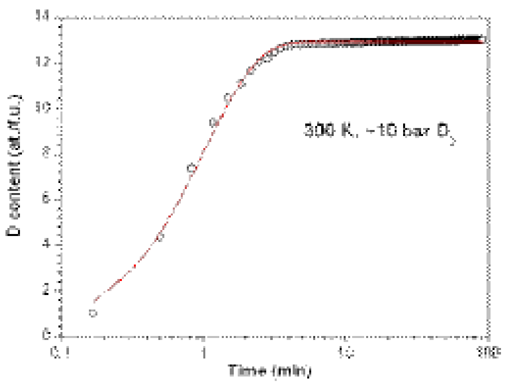
$(La,Pr,Nd)_{3-x}Mg_xNi_9$-H_2 SYSTEM



Composition/Unit cell	$Nd_2MgNi_9D_{12}$	$LaNdMgNi_9D_{12.5}$	$La_2MgNi_9D_{13}$
a, Å	5.3236(2)	5.3672(1)	5.4151(1)
c, Å	26.506(2)	26.602(2)	26.584(2)
V, Å³	650.56(7)	663.65(5)	675.10(6)
Δ*a*/*a*, %	6.9	7.2	7.6
Δ*c*/*c*, %	9.6	9.7	9.4
Δ*V*/*V*, %	25.3	26.1	26.7
P eq. (des.) bar	**1.2**	**0.4**	**0.04**

THERMODYNAMICS vs Mg CONTENT and La/Nd RATIO

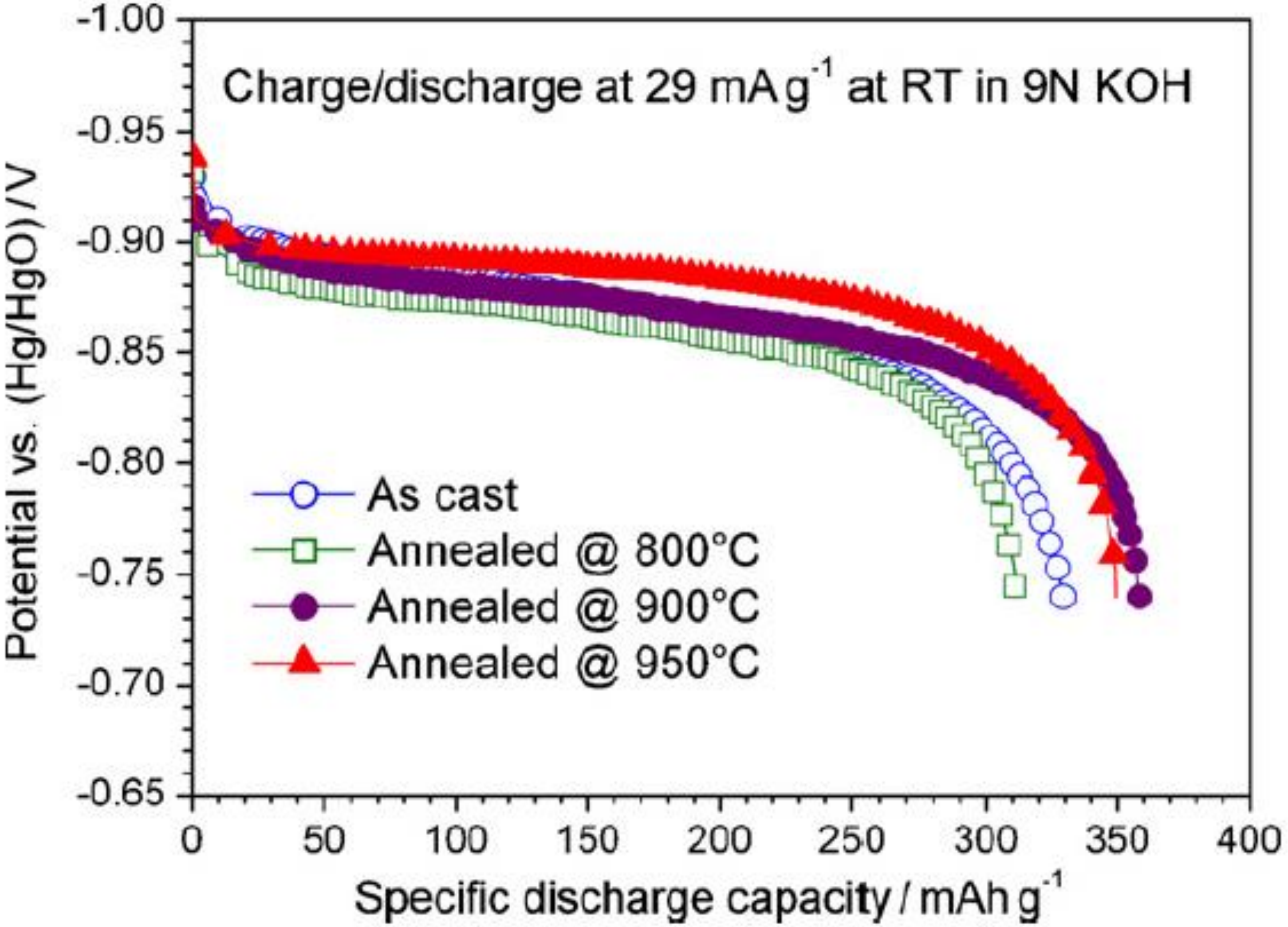
$La_{2.0}Mg_{1.0}Ni_9$ H ABSORPTION



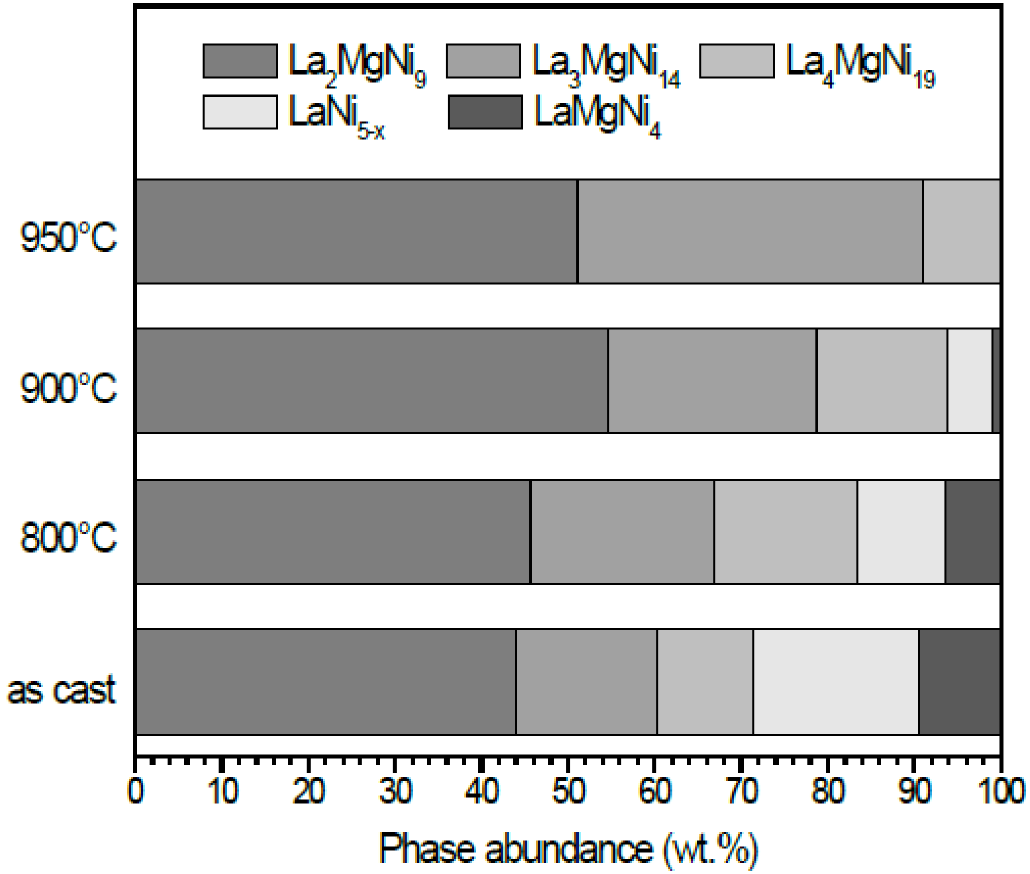
	ΔH, kJ/mol H_2
$La_{2.3}Mg_{0.7}Ni_9$	−37.4
$La_{2.0}Mg_{1.0}Ni_9$	−35.0±0.8
$La_{1.5}Mg_{1.5}Ni_9$	−29.2±1.2
$LaNdMgNi_9$	**-28.6±0.5**
Nd_2MgNi_9	**-24.0±0.7**
$La_{1.0}Mg_{2.0}Ni_9$	−22.5±0.3

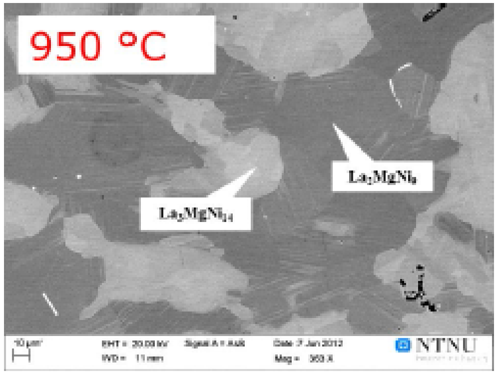
TUNING OF THE STABILITY CAN BE REACHED BY OPTIMISING Mg CONTENT AND RARE EARTH ELEMENT BETWEEN La, Nd and Pr

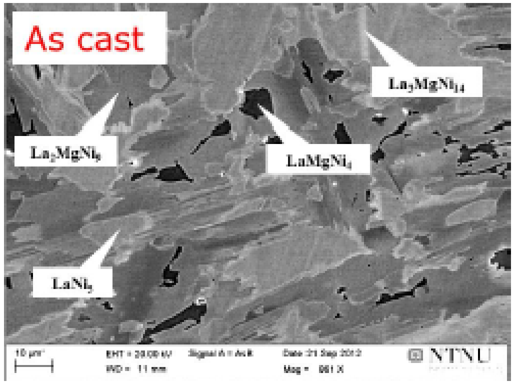
EFFECT OF HOMOGENISATION ON DISCHARGE PERFORMANCE OF La_2MgNi_9



Gradual decrease of the abundance of electrochemically inactive $LaMgNi_4$ and $LaNi_5$ which completely disappear at 950 °C

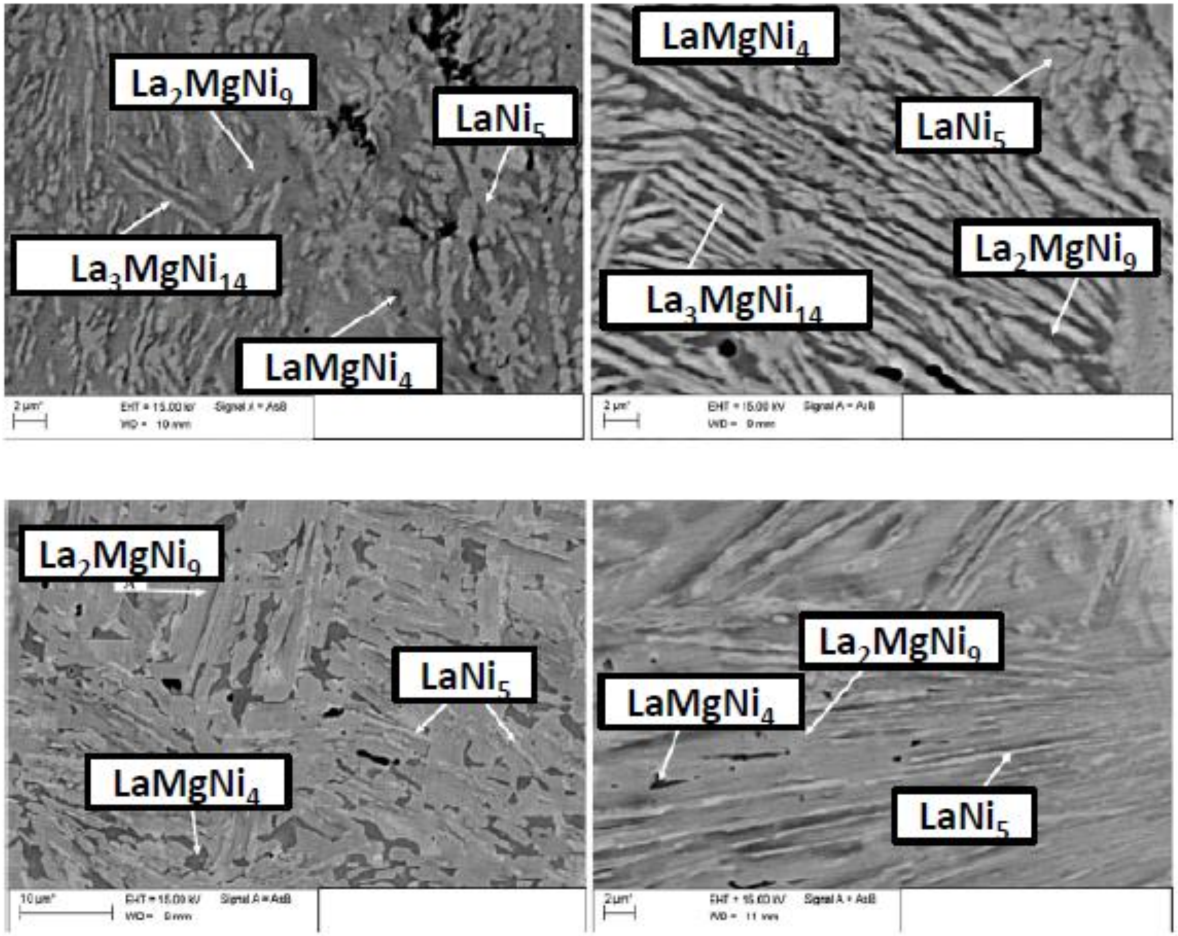






Wei-Kang Hu, Roman V. Denys, Christopher Nwakwuo, Thomas Holm, Jan Petter Maehlen, Jan Ketil Solberg and Volodymyr A. Yartys.// *Electrochimica Acta*, 96 (2013) 27-33.

EFFECT OF RAPID SOLIDIFICATION



La_2MgNi_9

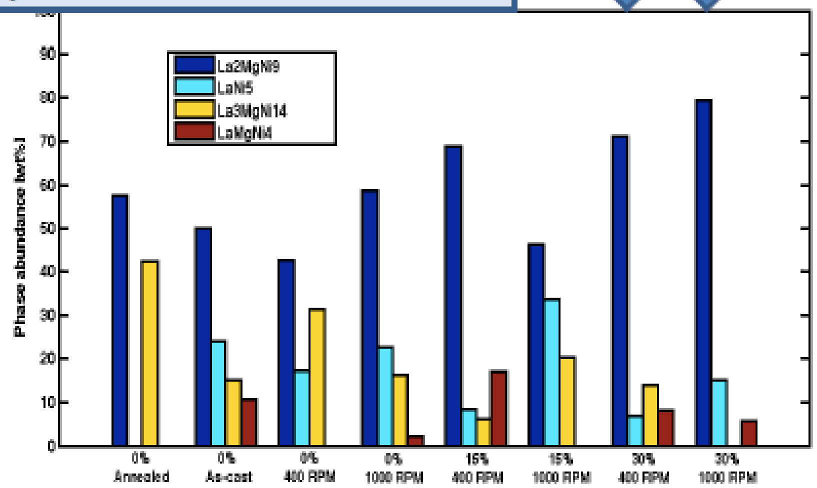
La_2MgNi_9 + 30 % Mg

$10.5\ mc^{-1}$ $4.2\ mc^{-1}$

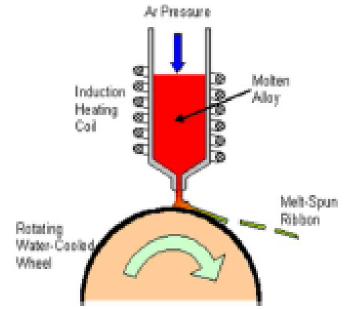
ADVANTAGES OF RAPID SOLIDIFICATION

La_2MgNi_9 + 30 % Mg ⟶ SUPPRESSES $LaNi_5$

EFFICIENT SYNTHESIS: yield 80 %



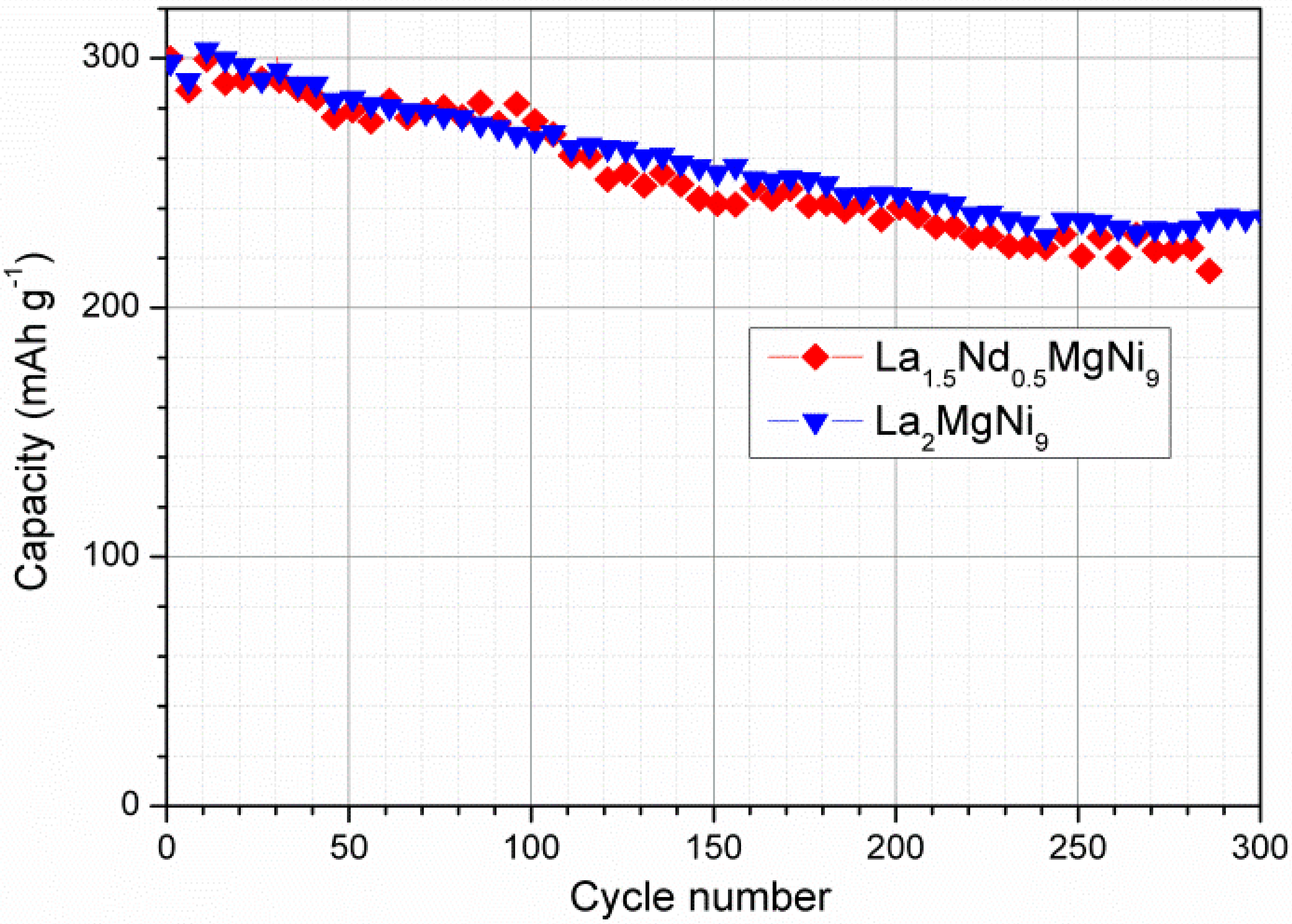
Ch.Nwakwuo, V.A. Yartys, et.al., JALCOM, 555 (2013) 201.



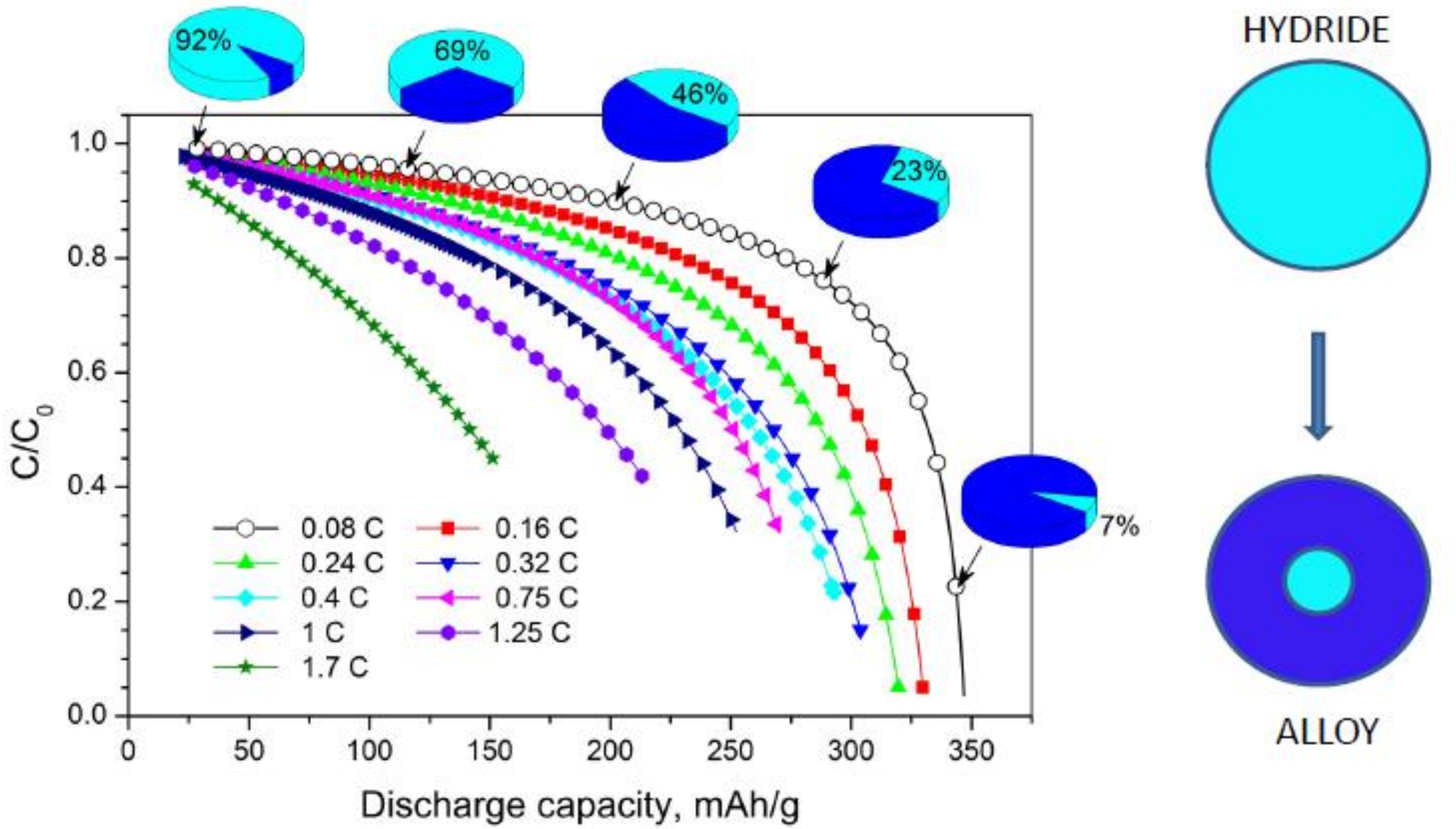
ELECTROCHEMICALLY ACTIVE → INCREASE La_2MgNi_9 + La_3MgNi_{14}

ELECTROCHEMICAL «BALLAST» → AVOID $LaNi_5$ + $LaMgNi_4$

HIGH CYCLE STABILITY

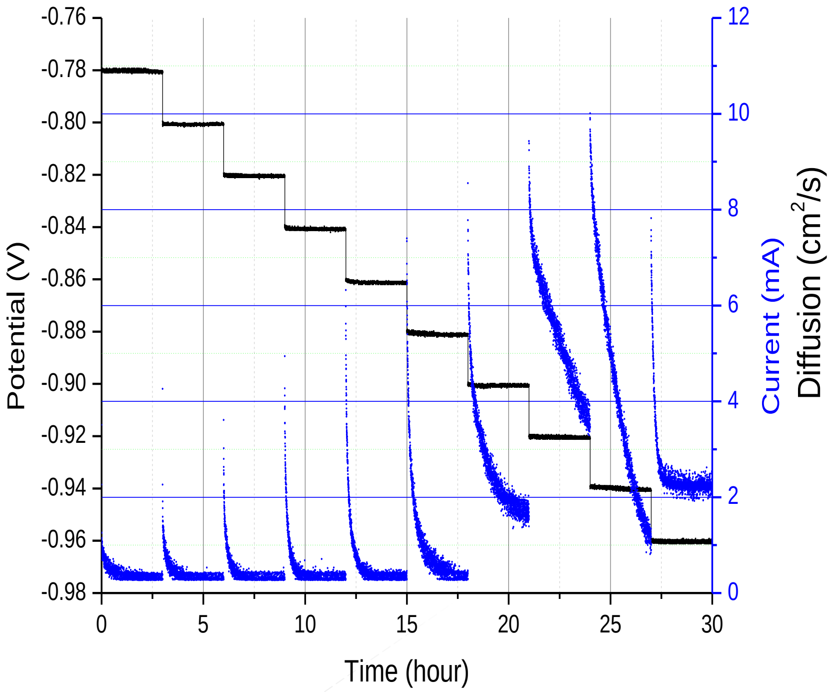


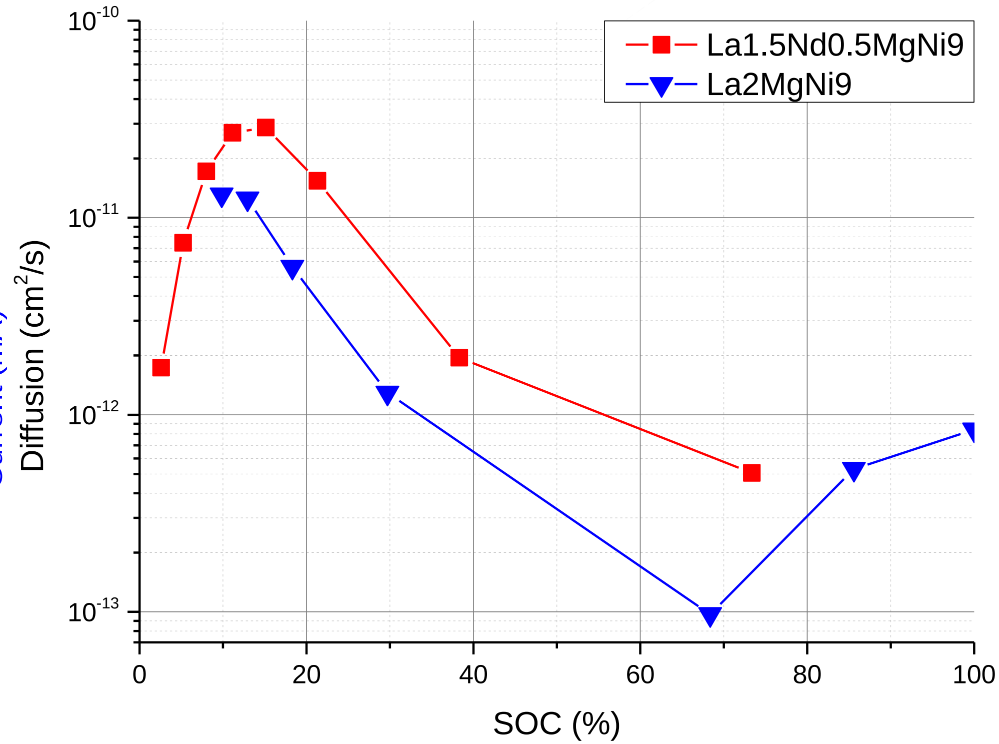
«SHRINKING CORE» MODELING



I.E. Gabis, E.A. Evard, A.P. Voyt , V.G. Kuznetsov, B.P. Tarasov, J.-C. Crivello , M. Latroche, R.V. Denys, Weikang Hu and V.A. Yartys. *ELECTACTA* (2014)

LOW AMPLITUDE CHRONAMPEROMETRY: H Diffusion in $La_{1.5}Nd_{0.5}MgNi_9$ and in in La_2MgNi_9





Cottrelian dependence

$$1/_{I\sqrt{t}} = {R_\Sigma}/_{\Delta E\sqrt{t}} + {l\sqrt{\pi}}/_{\Delta E\sqrt{D}C_{int}}$$

TIME RESOLUTION 3-5 MINUTES @ PSI SWITZERLAND

METAL HYDR.
AT PRESSURES UP TO 1000 BAR D2

COMMERCIAL BATTERY DURING CHARGE AND DISCHARGE

IN SITU STUDIES USING NEUTRON SCATTERING

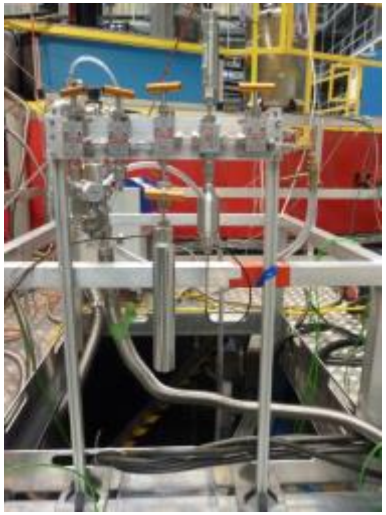
EQUILIBRIA IN MAGNESIUM ALLOYS AT TEMPERATURES UP TO 1000 C

METAL HYDRIDE BATTERY ANODES DURING CHARGE AND DISCHARGE

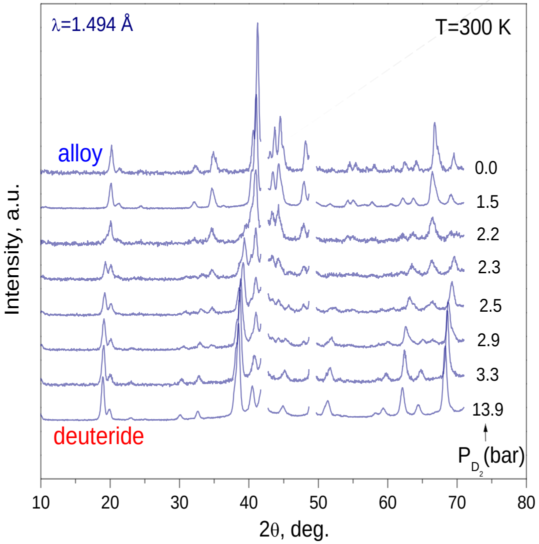
Neutron Diffraction: SINQ, PSI, Switzerland

High Resolution Diffractactometer: HRPT

Neutron wavelengths (0.94-2.96) Å. Range of 2θ=0-165° high Q ≤ 13 $Å^{-1}$. High resolution δd/d =10^{-3}



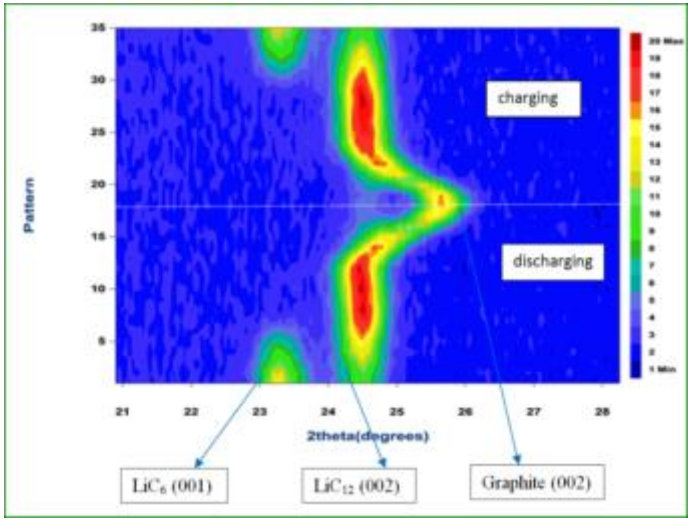
1000 bar hydrogenation rig

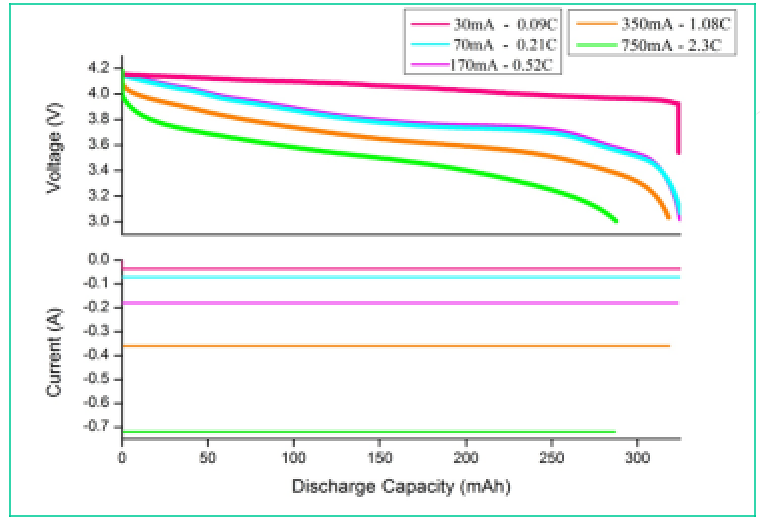


In situ NPD of isothermal desorption from $La_{1.5}Mg_{1.5}Ni_9D_{11}$

HIGH INTENSITY AND HIGH RESOLUTION DATA COLLECTED IN 3-5 MINUTES FOR ALL *d*-VALUES

HIGH POWER BATTERIES PROBED BY NEUTRON SCATTERING



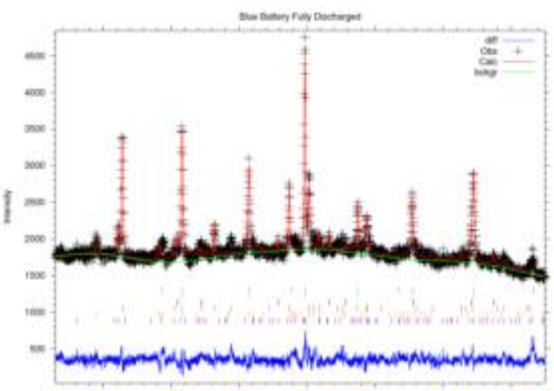


DISCHARGE:

LiC_6 / LiC_{12} → C (graphite)

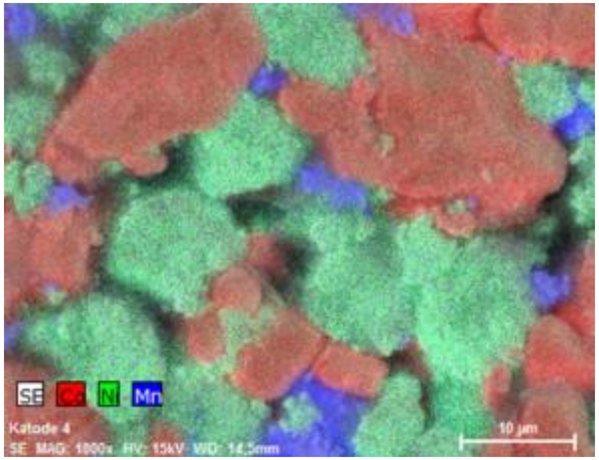
CHARGE:

C (graphite) → LiC_{12} → LiC_6



In situ charge/discharge data from SINQ neutron source, Paul Scherrer Institute, Switzerland.

NMC Li ION BATTERY

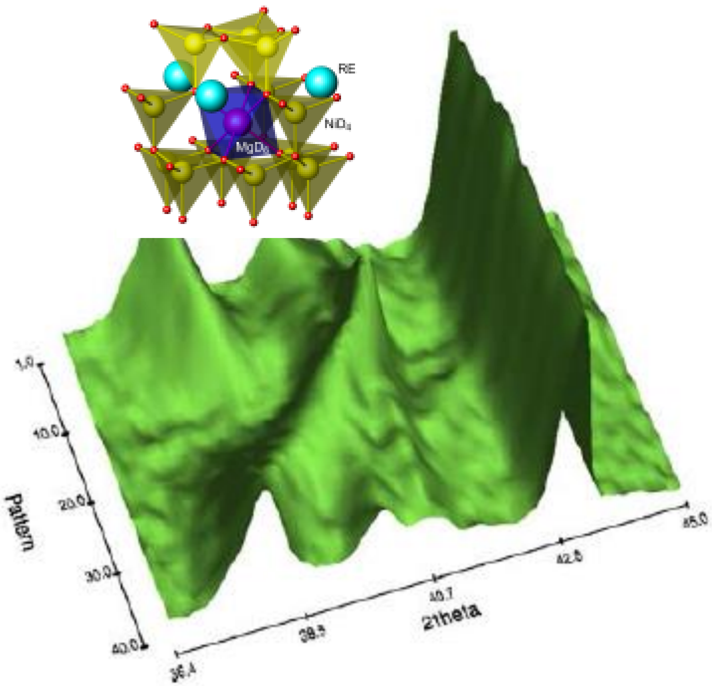


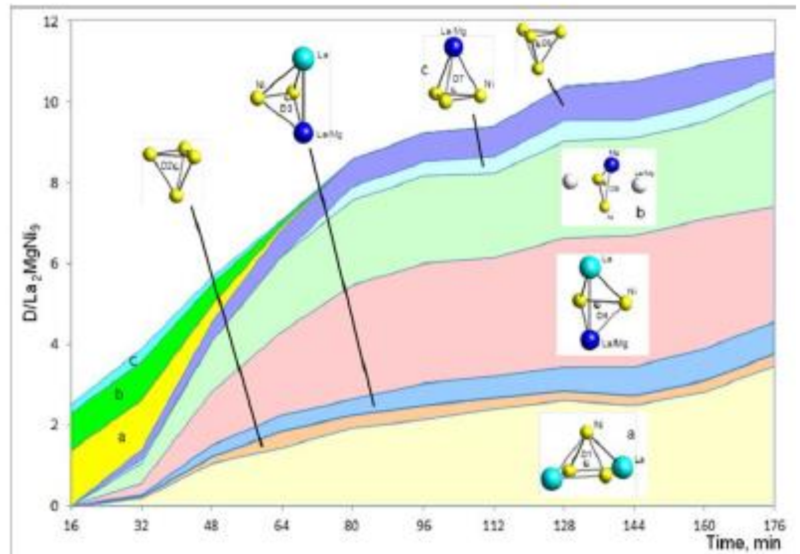
$Li_{1-x}(Ni,Mn,Co)O_2$ mixed oxide cathode

PhD project
Nazia S. Nazer
Cosupervisors
Lars Arnberg &
Volodymyr
Yartys

La_2MgNi_9 EL CHARGE-DISCHARGE (PSI)

Collaboration with Michel Latroche and Fermin Cuevas (ICMPE, CNRS, France)

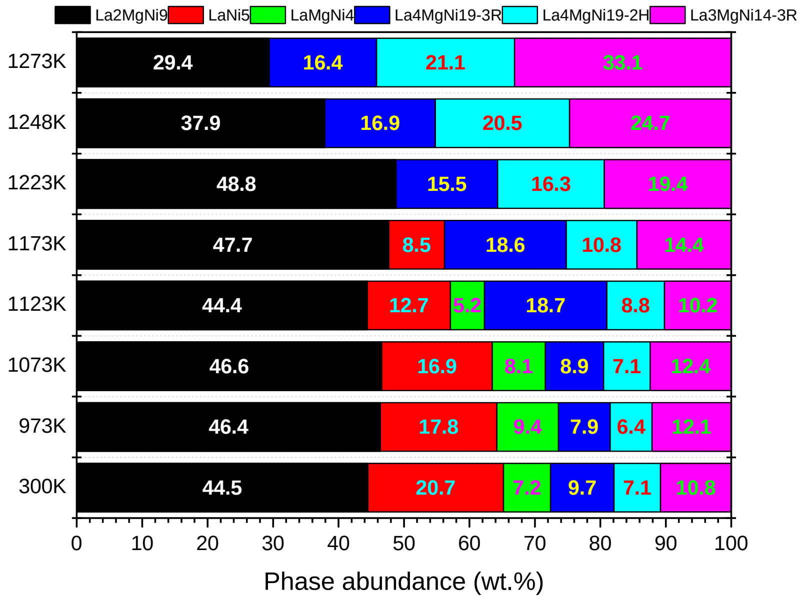


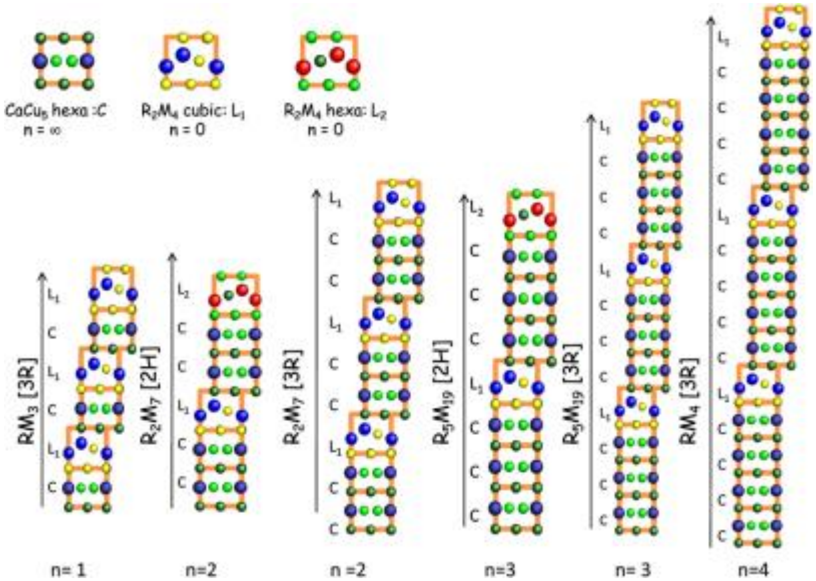


3D view of the ND pattern evolution as function of time during the first discharge-charge cycle (C/10) of the electrode La2MgNi9 at 150 mA.g^{-1}.

Michel Latroche, Fermìn Cuevas, Wei-Kang Hu, Denys Sheptyakov, Roman V. Denys and Volodymyr A. Yartys.
Mechanistic and kinetic study of the electrochemical charge and discharge of La_2MgNi_9 by in situ powder neutron diffraction.//
J. Phys. Chem. C, **2014**, *118* (23), pp 12162–12169. **DOI:** 10.1021/jp503226r.

HIGH TEMPERATURE IN SITU STUDIES @ ≤1000 C

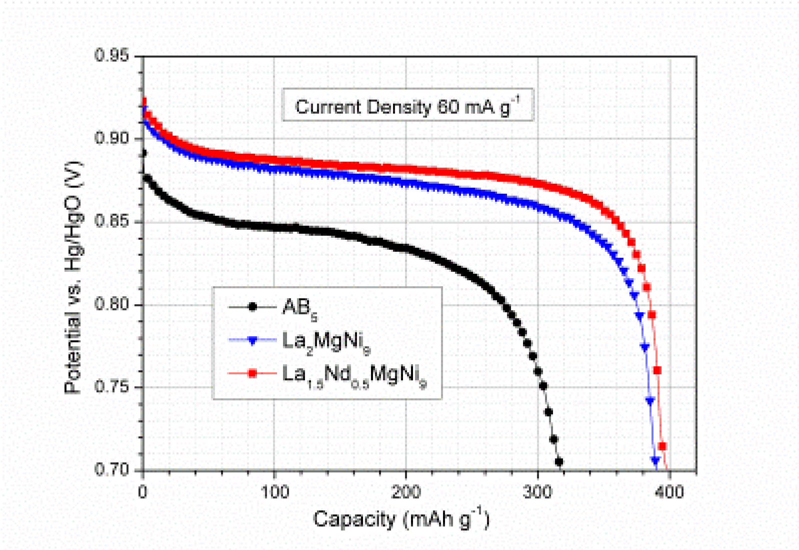


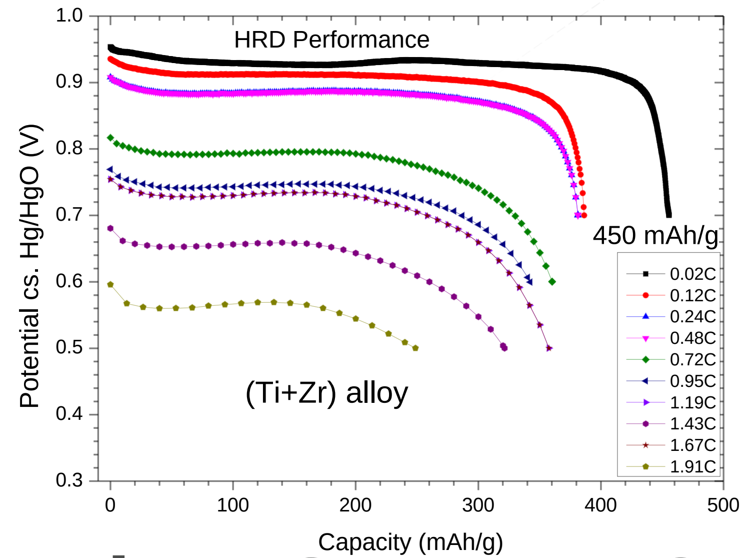


Dr. Chubin Wan

Dr. Roman Denys

STATUS AND FUTURE





Mg-BASED ALLOYS: >500 mAh/g

Ti-BASED ALLOYS: 450 mAh/g

IMPROVED Ni ELECTRODE

Dr. Chubin Wan
Dr. Alexey Volodin
Dr. Roman Denys

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Lars Arnberg	NTNU
Dag Noréus	Stockholm University, Sweden
Maximilian Fichtner	KIT, Germany
Denis Sheptyakov	PSI, Switzerland
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Fermin Cuevas	ICMPE, CNRS, France
Alexey Volodin	Russian AS
Boris Tarasov	Russian AS