HYDROGEN BASED ENERGY STORAGE USING METAL HYDRIDES

Volodymyr Yartys

22 February 2018

ERAfrica The Projects

New Knowledge Partnerships

Interfacing Challenges

New Ideas

Renewable Energies

New Knowledge Partnerships

8.29 Million €

17 Projects 65 Institutions

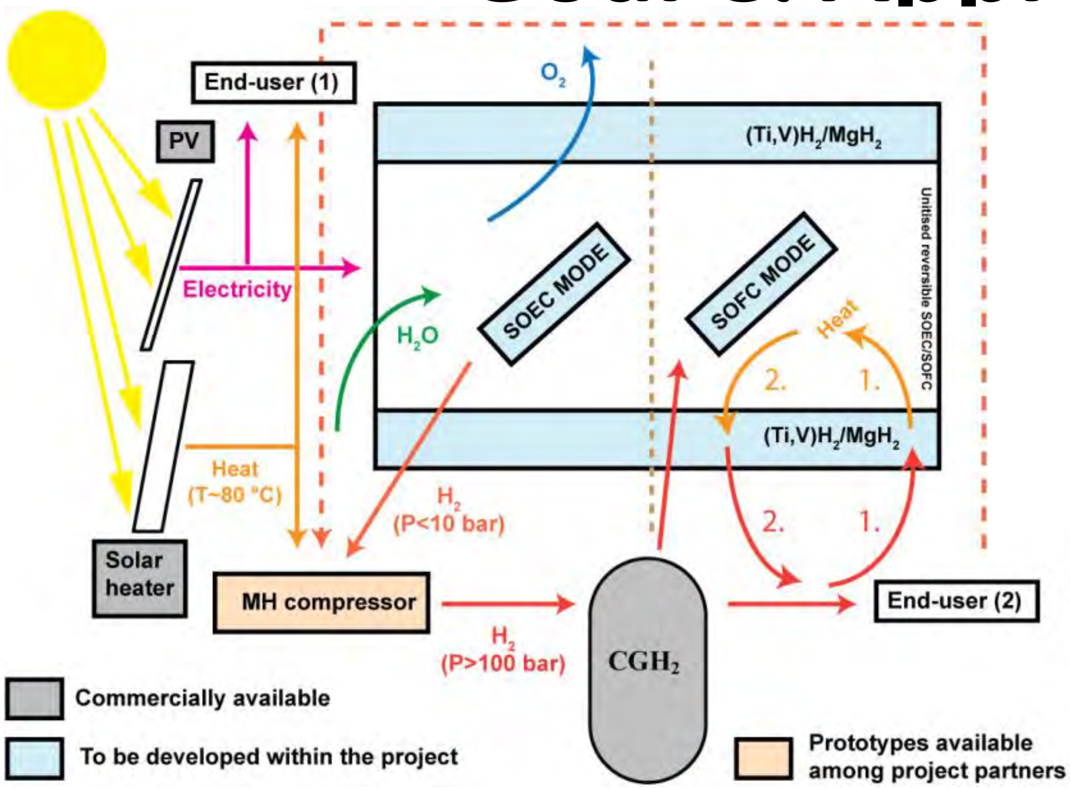
18 Participating Countries

ERAfrica is funded under FP7
Project number: FP-226154 | Programme: Capacities | Instrument: Coordination Action
http://www.erafrica.eu

The **HENERGY project** contributes to the thematic field "Renewable Energies" of the EU ERAfrica FP7 programme and aims to join the best efforts of the European and African scientific communities targeting development of the advanced hydrogen energy systems. The work is collaboration between the leading European and African research institutions: Institute for Energy Technology, Norway (IFE); Hydrogen Storage and Systems, Norway (HSS); Prototech AS, Norway (PRO); University of the Western Cape, South Africa (UWC), Middle East Technical University, Turkey (METU) and Cairo University, Egypt (CU).

IFE Institute for Energy Technology

Goal & Approach



The ultimate goal of the project is in creation of the prerequisites for the development of advanced energy systems utilising solar energy.

- Advanced integrated Unitised Reversible Fuel Cell System (U-RFCS) based on Solid Oxide (SO) technology;
- High temperature hydrogen storage and supply system operating at 300-550 °C.

Primary energy source: solar

Outputs:

- Electric power; → CHP
- Heat; → CHP
- Hydrogen. → HCHP

Electric power + heat management = Combined Heat and Power (CHP)

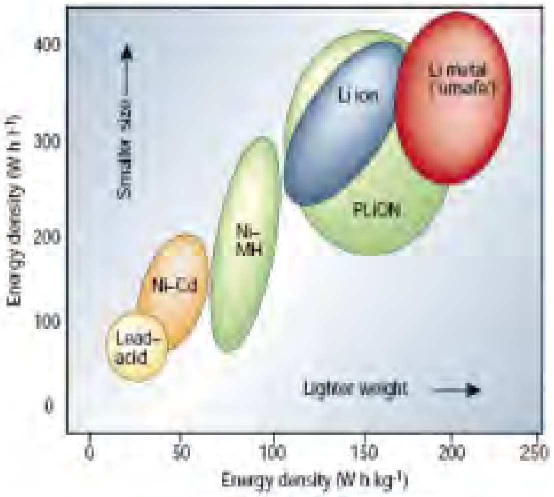
CHP → HCHP

CHP + H_2 production = HCHP

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

GOAL:

REDUCE / ELIMINATE USE
OF RARE EARTH METALS AND Co

INSTEAD OF $RE(Co,Ni)_5$

$(La, Pr, Nd)_2MgNi_9$

LAVES TYPE $(Zr/Ti)TM_2$

RARE EATH-Mg-Ni MH ANODE ALLOYS

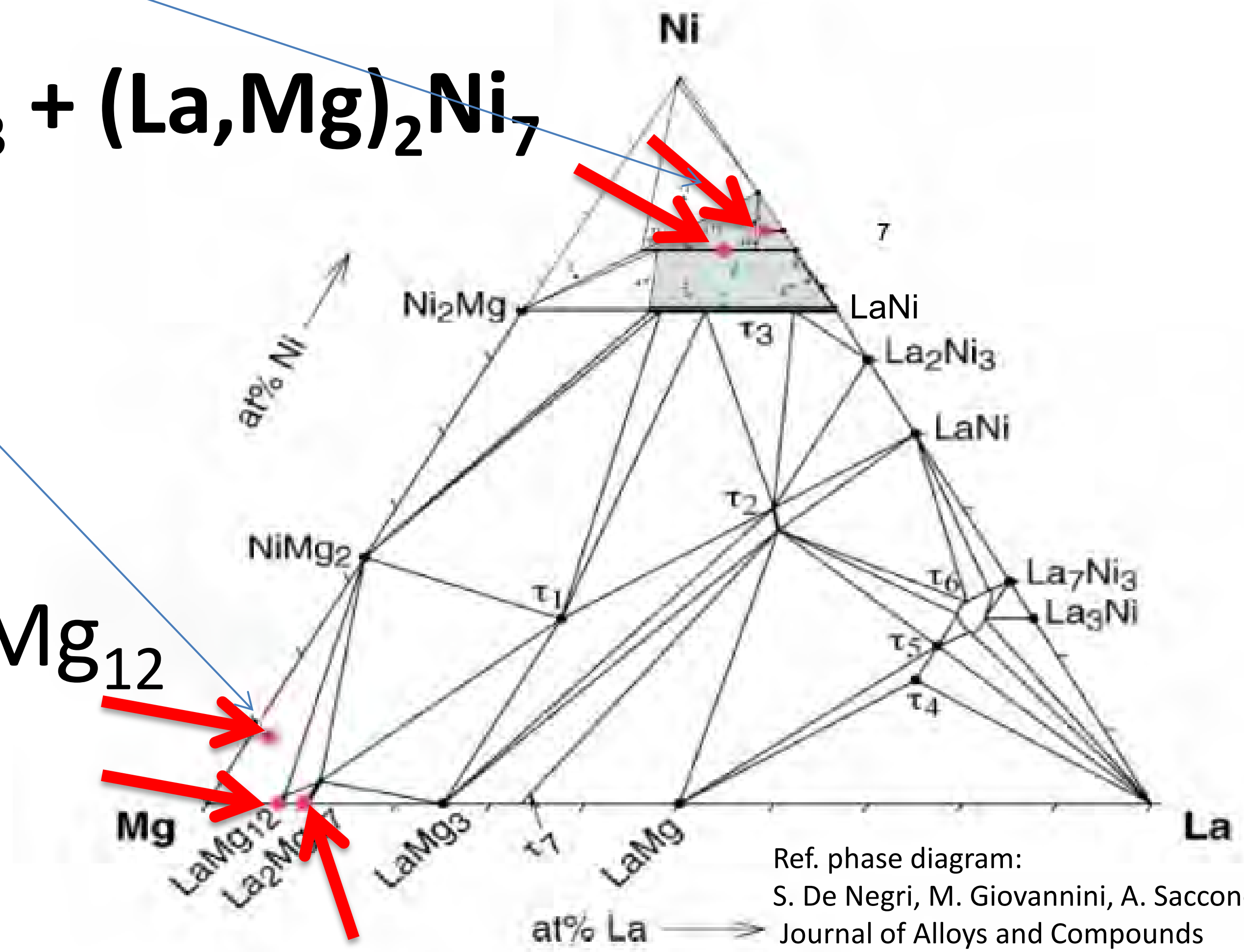
La-Mg-Ni Alloys

Ni-MH BATTERIES
La→Mg SUBSTIT.

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

H STORAGE/
FAST H KINETICS:
Mg METAL

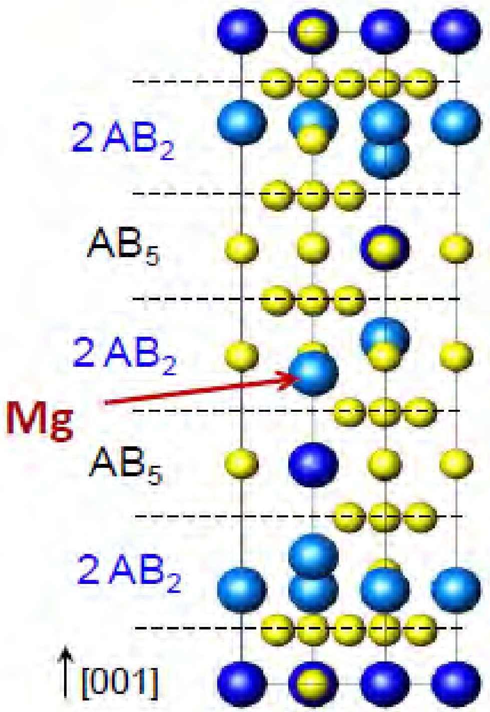
Eutectic
$Mg+Mg_2Ni+LaMg_{12}$
88 at% Mg



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

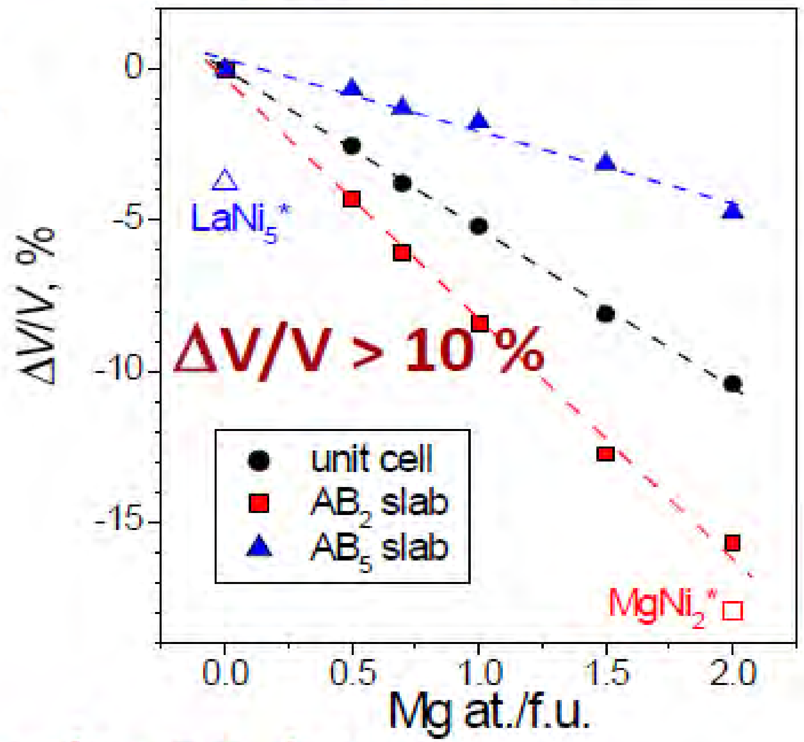
$LaMg_{12}$, $LaMg_{11}Ni$, $La_2(Mg,Ni)_{17}$

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



$r(\mathrm{La})=1.87$ Å
$r(\mathrm{Mg})=1.60$ 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)$_2$MgNi$_9$ BATTERY ANODES

Appl. Phys. A
DOI 10.1007/s00339-015-9538-9
Applied Physics A Materials Science & Processing
INVITED PAPER

Metal hydrides as negative electrode materials for Ni–MH batteries

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Received: 3 October 2015 / Accepted: 15 December 2015

Abstract Structural, thermodynamical and electrochemical properties of metallic hydrides belonging to the pseudo-binary family A–Mg–Ni (A: rare earths) are reviewed and compared. Technology aspects of bipolar cells are also discussed.

Hydrogen Based Energy Storage, in the area of the metal hydride batteries.

Metallic hydrides have been studied and developed during five decades for various energy storage and conversion systems (heat pumps, cryocooler, heat storage and batteries). Among these applications, the use of metal

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Electrochimica Acta
journal homepage: www.elsevier.com/locate/electacta

Modeling of metal hydride battery anodes at high discharge current densities and constant discharge currents

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[b] Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, 142432, RUSSIA
[c] Institut de Chimie et des Matériaux Paris-Est, UPEC-CNRS, UMR 7182, 2 rue Henri Dunant, Thiais, France
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ABSTRACT

In present work we have developed a theoretical model for the description of the electrochemical discharge process in the metal hydride anodes of the metal hydride batteries at various current densities. The model is based on the description of the assembly of the spherically shaped metal hydride particles where the process of electrochemical discharge is fit using a shrinking core model, with a shell of the H storage alloy growing inside the particle by decreasing volume of the internal metal hydride core. The model accounts results of the D.O.S. calculations for La$_2$MgNi$_9$ intermetallic alloy and has been tested for this metal hydride anode material having an electrochemical discharge capacity of 400 mAh/g and

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journal homepage: www.elsevier.com/locate/jpowsour

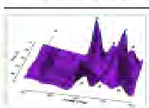
In operando neutron diffraction study of LaNdMgNi$_9$H$_{13}$ as a metal hydride battery anode

N.S. Nazer[a,b], R.V. Denys[a], V.A. Yartys[a,b,*], Wei-Kang Hu[a], M. Latroche[c], F. Cuevas[c], B.C. Hauback[a], P.F. Henry[d], L. Arnberg[b]

HIGHLIGHTS

- LaNdMgNi$_9$-D$_2$ system studied in operando by neutron diffraction.
- Nd substitution enhances the high rate discharge performance.
- H/M ratio is higher for the metal-D$_2$ gas system as for the electrochemical charging.
- Both alpha metal and beta deuteride phases have extended solid solution ranges.
- D atoms fill 7 types of interstitial sites.

GRAPHICAL ABSTRACT



Electrochimica Acta 96 (2013) 27–33
Contents lists available at SciVerse ScienceDirect
Electrochimica Acta
journal homepage: www.elsevier.com/locate/electacta

Annealing effect on phase composition and electrochemical properties of the Co-free La$_2$MgNi$_9$ anode for Ni-metal hydride batteries

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La-Mg-Ni alloy
Electrochemical energy conversion
Ni-MH battery

ABSTRACT

Present paper focuses on studies of the Co-free La$_2$MgNi$_9$ alloys as active materials of negative electrodes in nickel-metal hydride (NiMH) batteries. The effect of annealing treatment on the phase composition, microstructure, hydrogen absorption–desorption and electrochemical properties was investigated. The phase-structural composition, microstructures and morphologies of the phases were analyzed by X-ray diffraction and by scanning electron microscopy. Increase of the annealing temperature to 950 °C leads to a higher abundance of the La$_2$MgNi$_9$ and La$_3$MgNi$_{14}$ phases and an elimination of the present at lower temperatures LaNi$_{5-x}$ and LaMgNi$_4$ intermetallics. The hydrogen absorption–desorption behaviors, the electrochemical performance and electrochemical cycling stability significantly improve after the annealing. For pasted electrodes, the annealed alloys had a discharge capacity of 350–360 mAh g^{-1} compared to 325 mAh g^{-1} for the as-cast sample. The discharge capacity of the annealed samples remained high, almost 50% after 300 cycles with 100% depth of discharge (DOD) in half-cell tests. Pellet electrodes prepared from the annealed alloy and carbonyl nickel powder showed a discharge capacity of 396 mAh g^{-1}. In present work we also report the performance of a small prototype NiMH cell where the annealed alloy was used as the active material in the negative MH electrode and a sintered Ni electrode acted as the positive electrode. After 300 cycles at charge/discharge rates of 0.2 C the cell showed a very good cycling stability with its capacity remaining on the level of 87%.

Mechanistic and Kinetic Study of the Electrochemical Charge and Discharge of La$_2$MgNi$_9$ by in Situ Powder Neutron Diffraction

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[‡] Institute for Energy Technology, Department of Energy Systems, 2007 Kjeller, Norway
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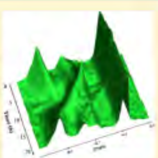
[∥] Norwegian University of Science and Technology, 7491, Trondheim, Norway

Supporting Information

ABSTRACT: The intermetallic La$_2$MgNi$_9$ has been investigated as negative electrode material for NiMH battery by means of in situ neutron powder diffraction. This hydride-forming compound exhibits suitable plateau pressures ranging within the practical electrochemical window and leads to significant reversible electrochemical capacities. Charge and discharge of the composite electrode have been performed in beam following various current rates and galvanostatic intermittent titration. From the diffraction data analysis, phase amounts and cell volumes have been extracted, allowing the interpretation of the hydride formation and decomposition. From the evolution of the diffraction line widths, differences are observed between charge and discharge with the possible formation of an intermediate γ phase on charge. The electrode readily responds to current rate variations and does not show any kinetic limitation in the range C/10 and C/5 (C/n: full capacity C in n hours). This material shows excellent properties regarding electrochemical storage of energy.



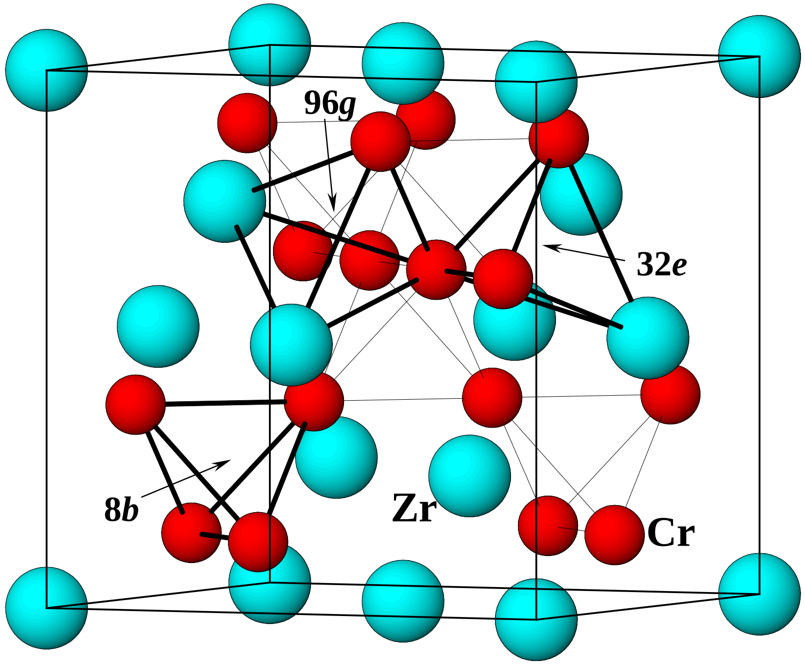
400 mAh/g

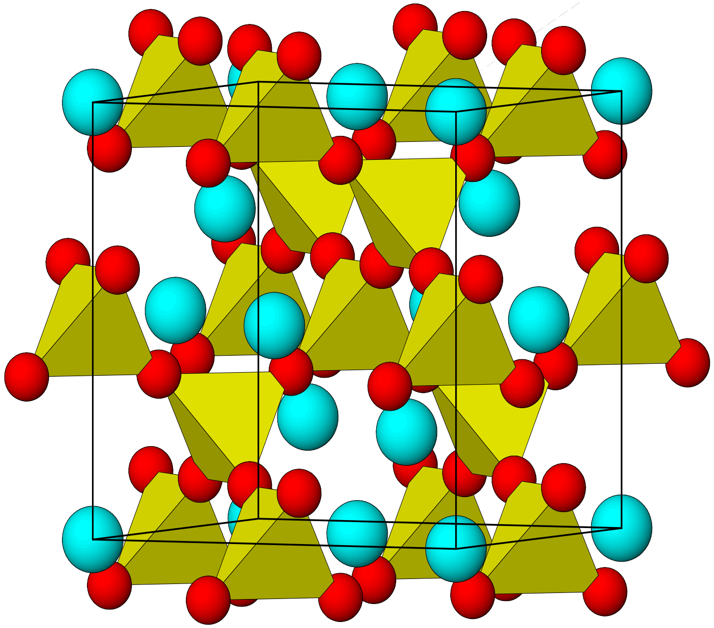
>300 cycles

Adjustable stability and diffusion rate by La/Pr/Nd

Zr/Ti BASED MH ANODE ALLOYS

C15 Laves type structure





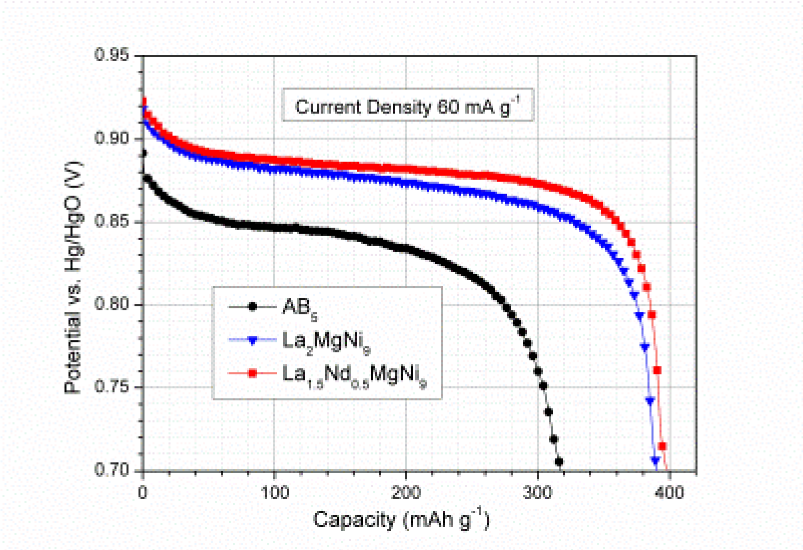
8*a* site: A, A+B;   16*d* site: B

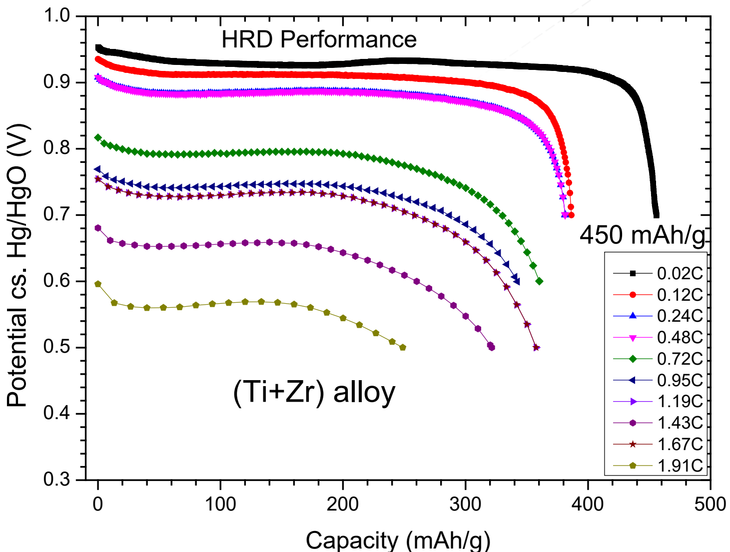
A_2B_2 – 96; AB_3 – 32; B_4 – 8

STRATEGY IN THE SELECTION OF THE Zr/Ti BASED MH ANODE ALLOYS

- Use Laves type solid solutions between $TiTM_2$ and $ZrTM_2$
- H_2 equilibrium pressure should be close to 1 bar
- C15 / C14 structures
- Stoichiometric TM/(Ti+Zr) = 2 as compared to the overstoichiometric compositions with TM/(Ti+Zr) > 2
- Cyclic stability as related to Ti / Zr content
- Choice of transition metals: Ni / Mn / V / Fe
- Achieve easy activation of the alloys

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

***In operando* neutron scattering investigation of a commercial Li-ion battery at variable current densities**

TIME RESOLUTION 3-5 MINUTES @ PSI SWITZERLAND

METAL HYDR.
AT PRESSURES UP TO 1000 BAR D2

COMMERCIAL BATTERY DURING CHARGE AND DISCHARGE

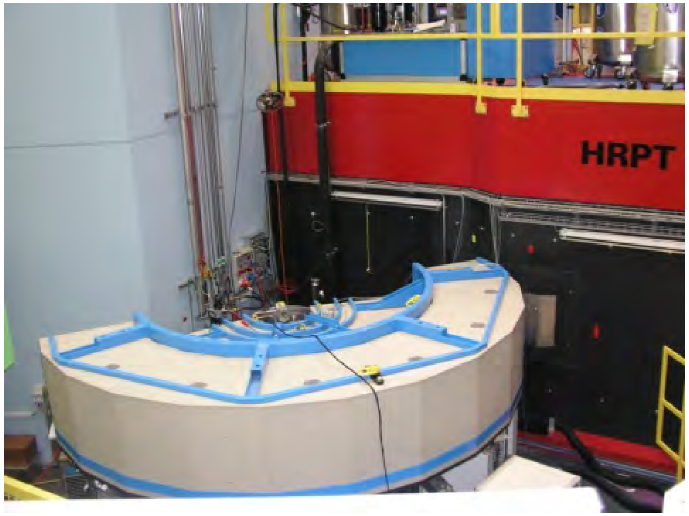
IN SITU STUDIES USING NEUTRON SCATTERING

EQUILIBRIA IN MAGNESIUM ALLOYS AT TEMPERATURES UP TO 1000 C

METAL HYDRIDE BATTERY ANODES DURING CHARGE AND DISCHARGE

LARGE SCALE FACILITIES: FREE ACCESS VIA QUALITY PROPOSALS

In situ powder diffraction (SXRD, NPD)



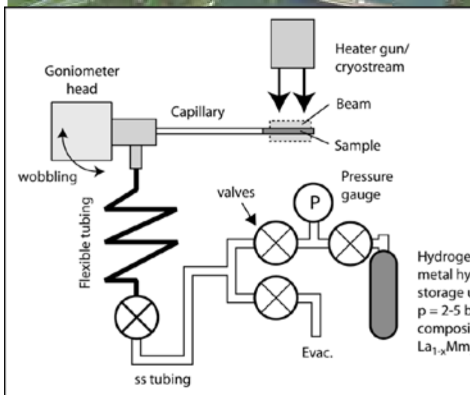
SXRD
SNBL, ESRF, France

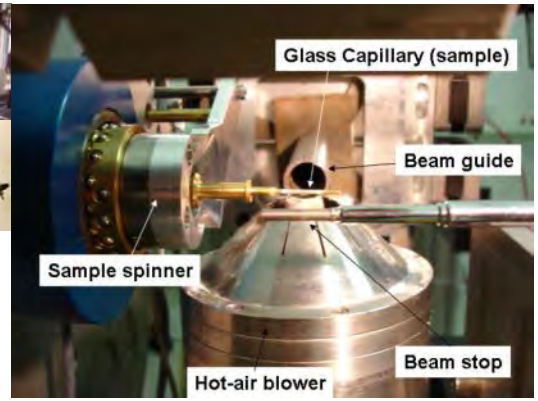
PND
D1B @ ILL, Grenoble
SINQ, PSI, Switzerland

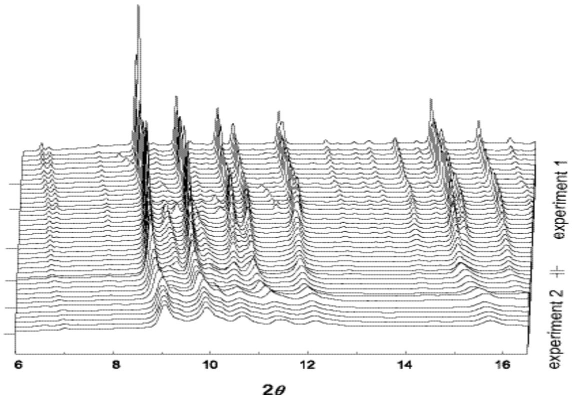
HIGH FLUX BEAM. 10^6 MORE INTENCE AS COMPARED TO A CONVENTIONAL DIFF

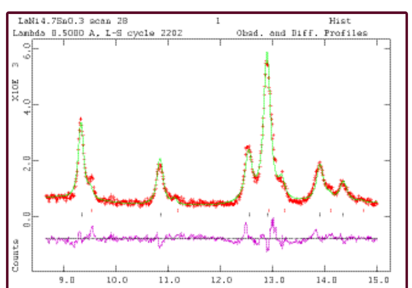
PROBING OF THE KINETICS AND MECHANISM OF THE METAL-HYDROGEN INTERACTIONS

In situ studies:
Swiss-Norwegian Beam Line, ESRF
50 bar H_2 / vacuum @ 800 °C
Gas mixtures: H_2+CO; Cryostream;
High pressures (GPa)

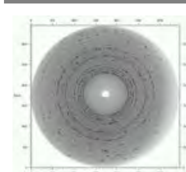


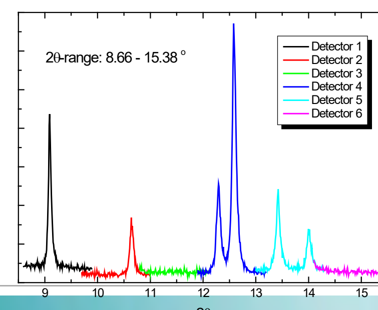






BM01





BM31

Tantalum furnace

375K ... 1400K

Sample holder

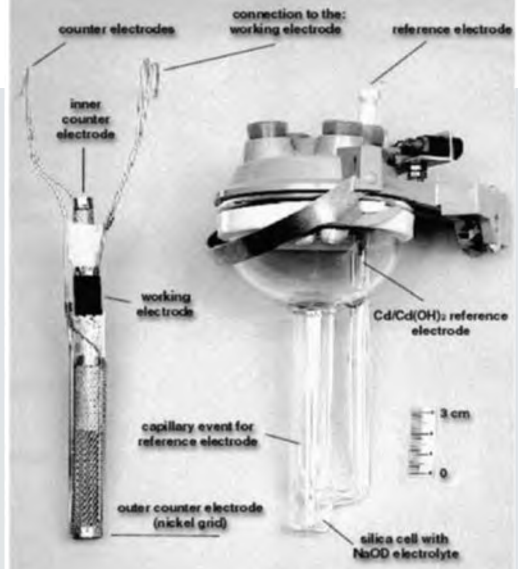
diam.: 50mm

Orange cryostat

1.5...320 K

Sample holder

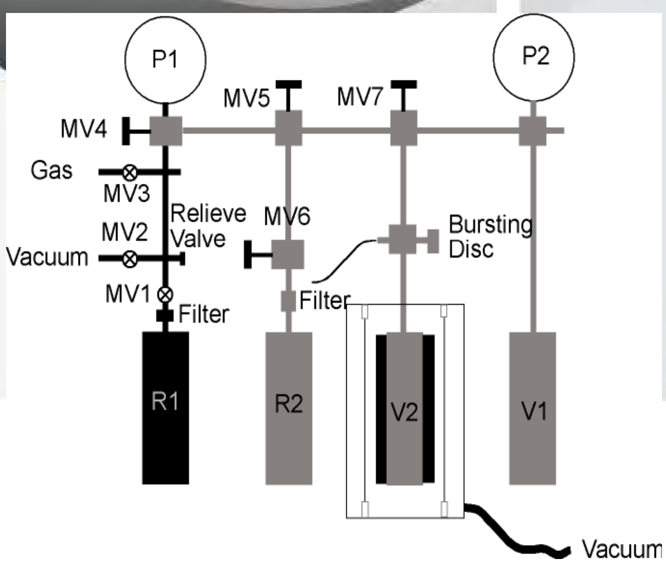
diameter: 50 mm



Electrochemical cell mounted on the HRPT diffractometer at Paul Scherrer Institute

Collaboration wiith ICMPE, CNRS, France

Dr. M. Latroche and Dr. F. Cuevas



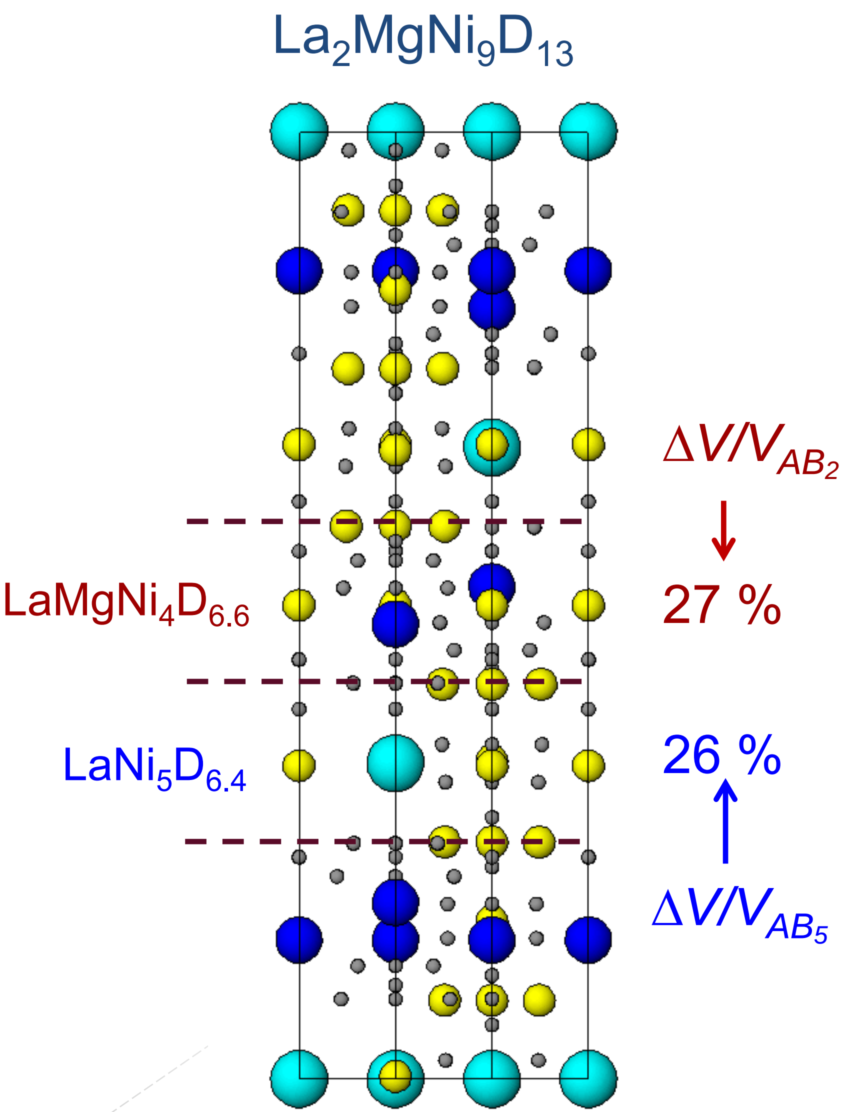
High pressure Zr-Ti sample cell

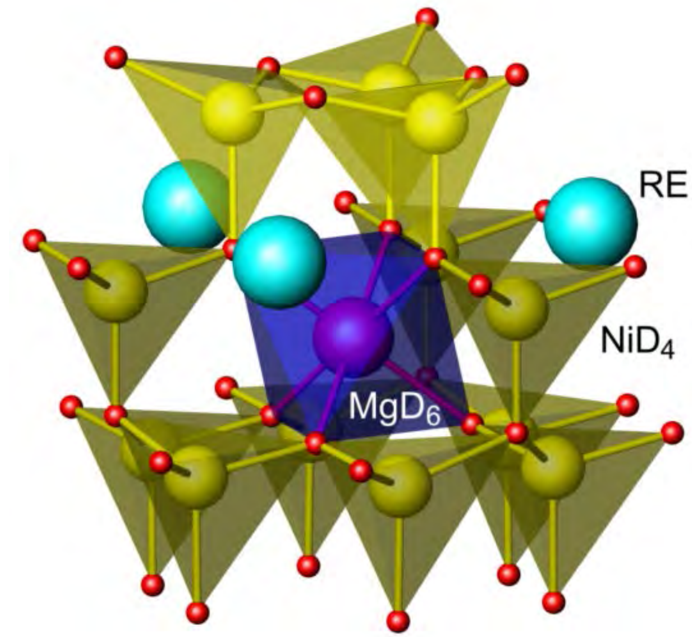
Collaboration with Griffith University, Australia

Prof. Evan Gray, Dr. Jim Webb, Dr. Timothy Webb

IFE

Structures of $La_{3-x}Mg_xNi_9$ hydrides

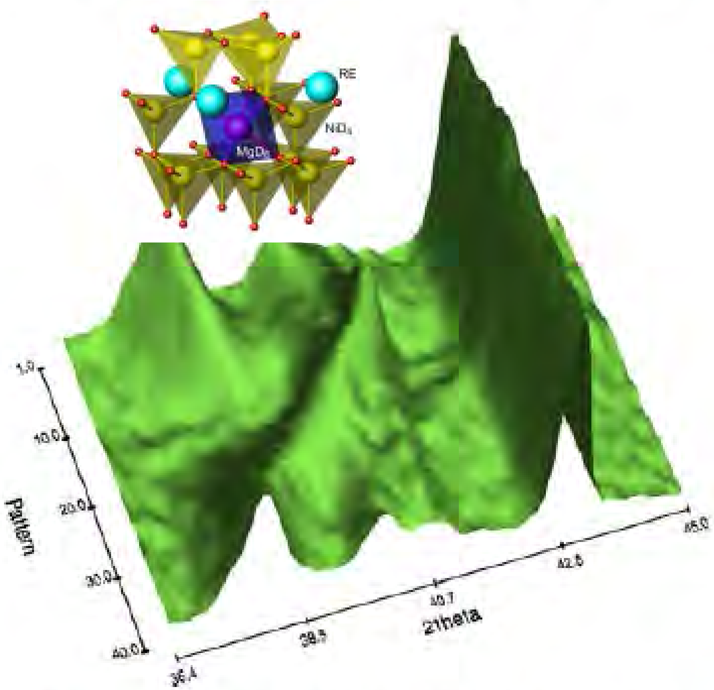


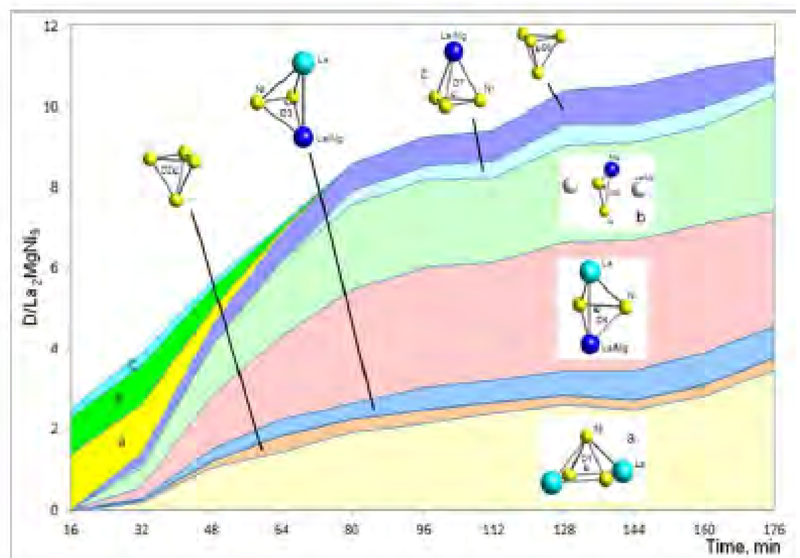


Filling of both AB_5 and AB_2 layers at all Mg/La substitutions

La_2MgNi_9 EL CHARGE-DISCHARGE (PSI)

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

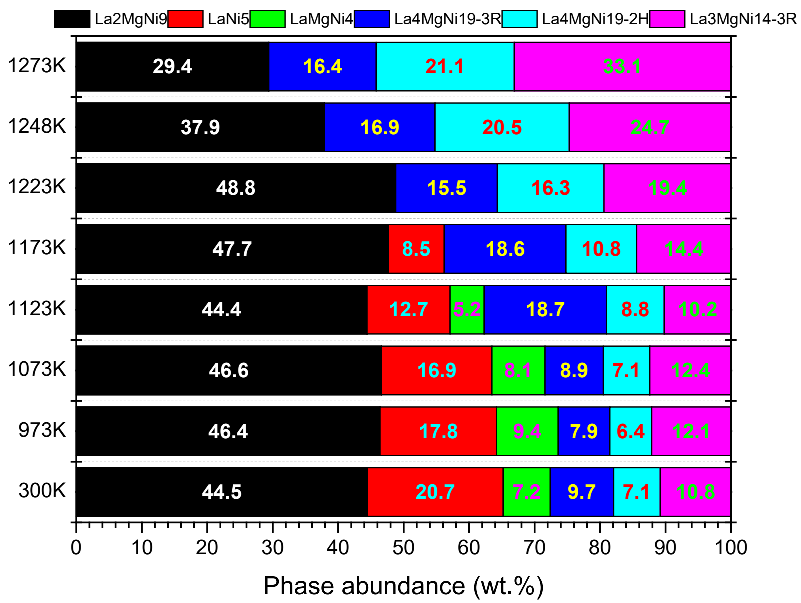


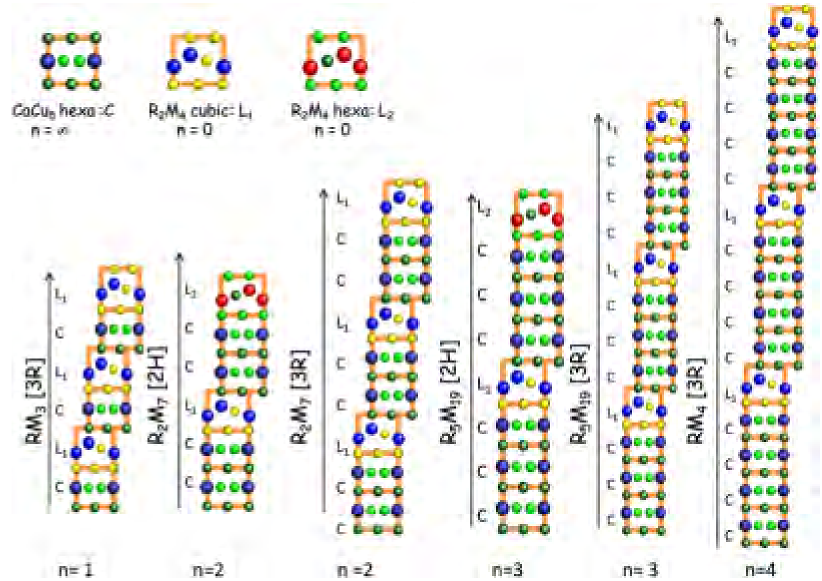


3D view of the ND pattern evolution as function of time during the first discharge-charge cycle (C/10) of the electrode La2MgNi9 at 150 mA.g^{-1}.

Michel Latroche, Fermin 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

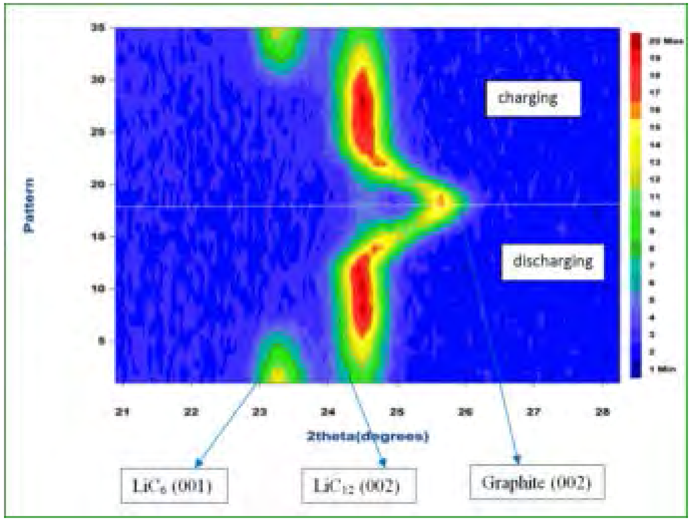


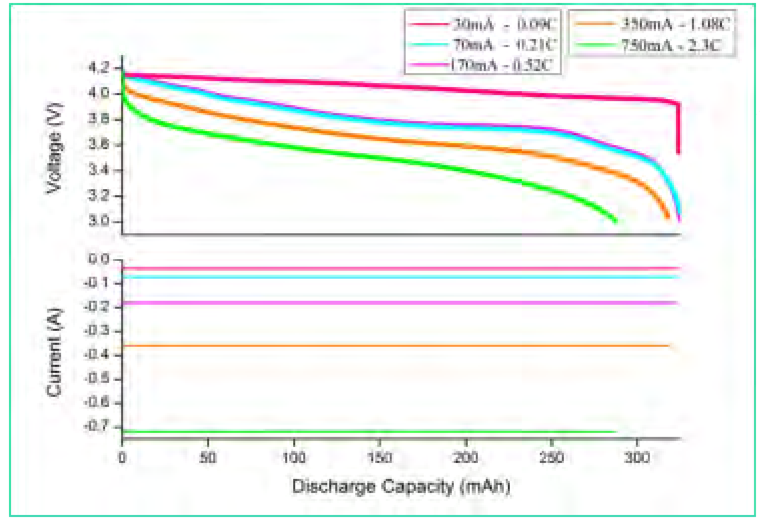


Dr. Chubin Wan

Dr. Roman Denys

HIGH POWER BATTERIES PROBED BY NEUTRON SCATTERING





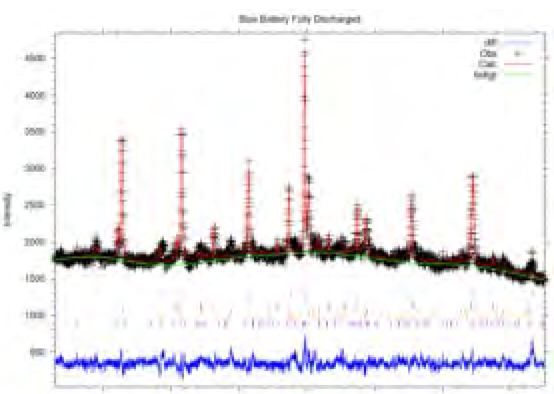
DISCHARGE:

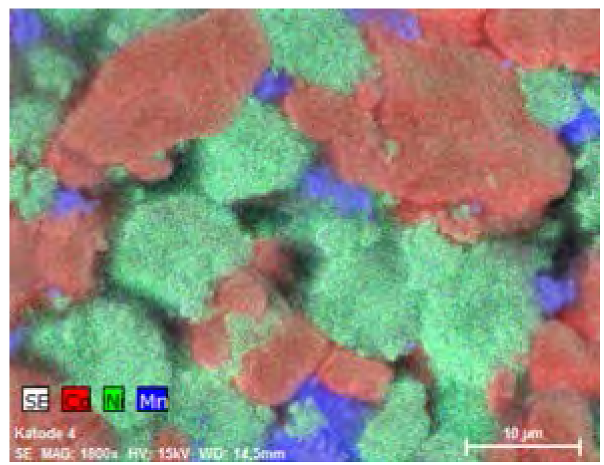
LiC_6 / LiC_{12} → C (graphite)

CHARGE:

C (graphite) → LiC_{12} → LiC_6

NMC Li ION BATTERY

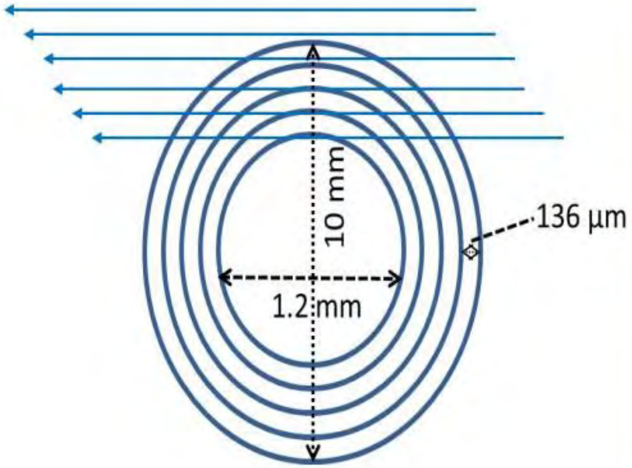


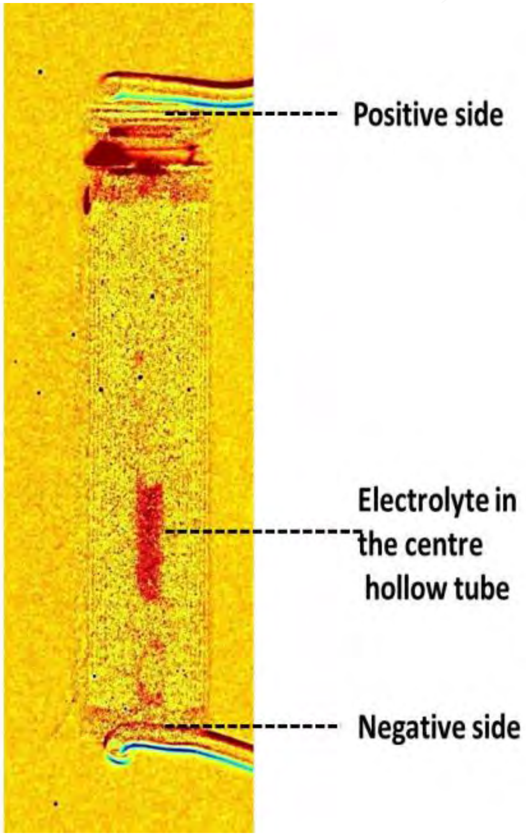


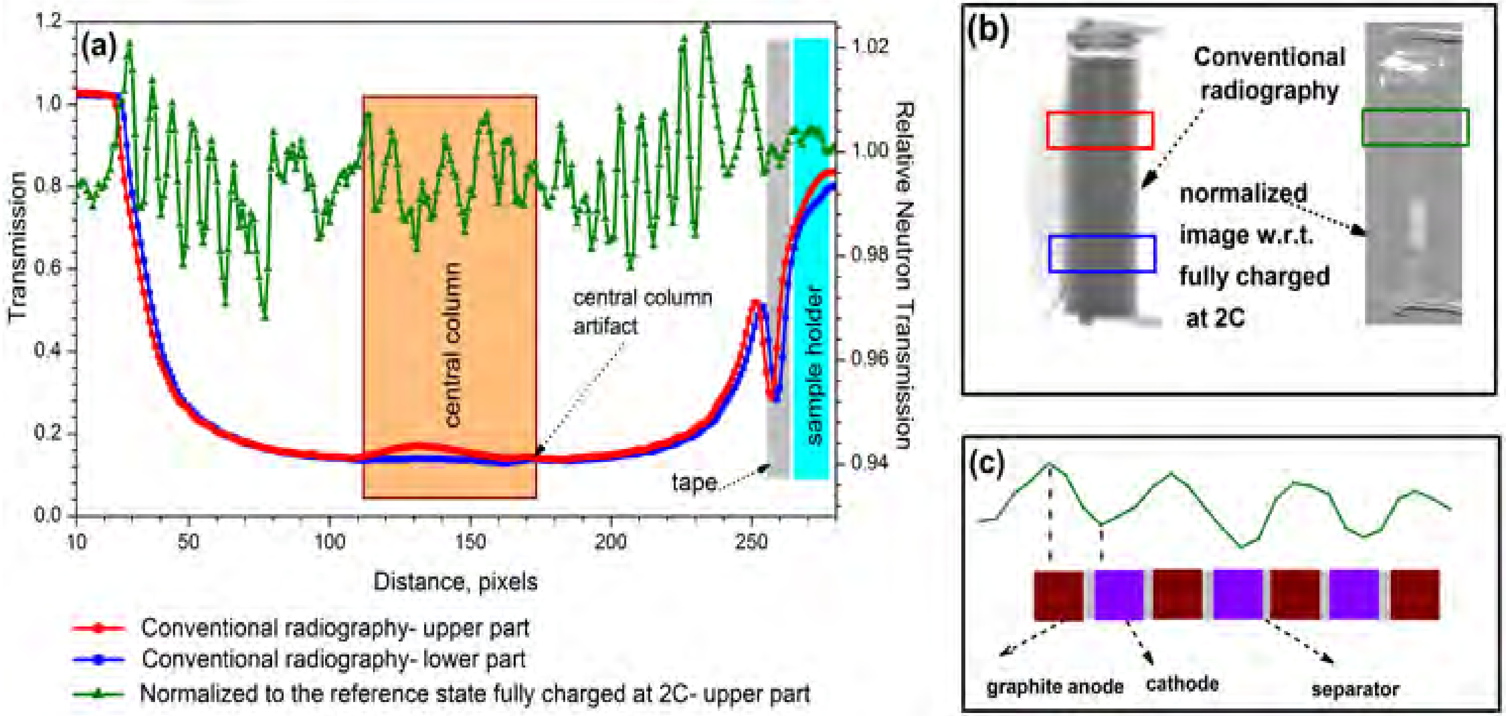
In situ charge/discharge data from SINQ neutron source, Paul Scherrer Institute, Switzerland.

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

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


10 mm
136 µm
1.2 mm


Positive side
Electrolyte in
the centre
hollow tube
Negative side


(a)
Transmission
Relative Neutron Transmission
Distance, pixels
central column
central column artifact
sample holder
tape
Conventional radiography- upper part
Conventional radiography- lower part
Normalized to the reference state fully charged at 2C- upper part
(b)
Conventional radiography
normalized image w.r.t. fully charged at 2C
(c)
graphite anode
cathode
separator

Thank you for your attention