

Introductory words



Michel Latroche, internationally recognized as a pillar of the hydride community, and more generally of research on the fundamental properties of materials for energy applications, passed away suddenly on December 30, 2021. This international day, which aims to outline the broad panorama of his research interests, is dedicated to his memory.

Michel Latroche's research activities have been mainly devoted to the study of alloys, intermetallic compounds, rare earths and porous materials having the property of reacting with hydrogen to form various compounds with remarkable structural, thermodynamic, physical and electrochemical properties. These hydrogenated materials are attracting ever-increasing interest, both fundamentally and applied. Indeed, they are able to store hydrogen and its isotopes under tuneable pressure and temperature conditions. They are currently used as electrode materials in commercial Ni-MH batteries and are being considered as electrode and electrolyte materials for future generations of Li-ion batteries.

This day counts with the contribution of numerous international and national collaborators of Michel Latroche, all internationally recognized in their field of expertise. Through their scientific presentations and their personal testimonies, we will have the opportunity to learn more about the challenges and achievements of Michel Latroche's career in the fields of solid-state chemistry, hydrogen storage and electrochemical energy storage.

At this step, we would like to thank the different institutions that have supported this event:

- the Institute National of Chemistry (INC) of the CNRS
- the University Paris-Est Créteil
- the French Research Network for Hydrogen Energy (FRH2)
- the Institut de Chimie et des Matériaux Paris-Est (ICMPE)

Finally, we have to mention the emotion we had in the preparation of this event. Thank you Michel for your support, your involvement in the laboratory and your scientific contribution to the field of metal hydrides.

The organizing committee:

- Dominique Alain
- Gladys Bernari
- Jean-Claude Crivello
- Fermín Cuevas
- Jean-Marc Joubert
- Mickaël Mateos
- Judith Monnier
- Valérie Paul-Boncour
- Karine Provost
- Junxian Zhang
- Claudia Zlotea



Program

Start	End	Session or Presentation Title	Chairs or Speakers
09:00	09:25	Welcome & Coffee	
09:25	09:30	Introduction to the workshop	Fermin Cuevas
09:30	10:30	Institutional Session: a memorial to Michel Latroche	Chairs: Jean-Marc Joubert, Fermin Cuevas
		A short biography of Michel Latroche	Jean-Marc Joubert, Fermin Cuevas
		ICMPE: East Paris Institute of Chemistry and Materials	Ivan Guillot
		UPEC-EDSIE: Université Paris-Est Créteil- Doctoral School	Valérie Langlois
		INC: The CNRS Institute of Chemistry	Alexandre Legris
		FRH2: the French Research network on H2 energy	Olivier Joubert
		International Hydride Community	Jacques Huot
10:30	12:00	Scientific Session I: Solid state chemistry	Chairs: Jean-Claude Crivello / Karine Provost
		In situ studies of phase-structural transformations in hydrogen and energy storage materials: an overview	Volodymyr Yartys, IFE, Norway
		The solid-state chemistry-application duality	Jean-Louis Bobet, CNRS/ICMCB, France
		New Mg ²⁺ ionic conductors in the Mg-B-N-H system	Raphael Janot, CNRS/ LRCS, France
		Plastic crystals built from (carba-) boron clusters Lego - excellent solid-state electrolytes	Radovan Černý, Univ. Geneva, Switzerland
		Crystal chemistry of Li ₃ PS ₄ and Na ₃ PS ₄ , solid electrolytes for batteries	Christian Masquelier, UPJV/LRCS, France
12:00	14:00	Lunch	
14:00	15:30	Scientific Session II: Solid state hydrogen storage	Chairs: Valérie Paul-Boncour / Claudia Zlotea
		Applications for metal hydrides - current projects and challenges	Klaus Taube, Hereon Institute, Germany
		In situ neutron diffraction investigation of Mg-Ni alloys processed by fast-forging	Patricia de Rango, CNRS/Néel, France
		HyCARE: we care about hydrogen!	Marcello Baricco, Univ. Turin, Italy
		Metal tritide: aging studies	Sylvain Challet, CEA Valduc, France
		Enthalpy-entropy compensation in BCC and high entropy alloys	Jacques Huot, Univ. QRT, Canada
15:30	16:00	Coffee Break	
16:00	17:30	Scientific Session III: Electrochemical energy storage	Chairs: Judith Monnier / Junxian Zhang
		Hydride-based batteries, past and future	Petra de Jongh, Univ. Utrecht, The Netherlands
		Use of hydride based materials in all solid state batteries	Christian Jordy, SAFT Batteries, France
		Metal hydrides as electrolytes for solid state batteries	Torben Jensen, Univ. Aarhus, Denmark
		Original mechanisms highlighted by XRD and absorption spectroscopy performed operando upon cycling of Na ₃ V ₂ (PO ₄) ₂ F ₃ and Na ₃ V ₂ (PO ₄) ₃ in Na-ion batteries	Laurence Croguennec, CNRS/ICMCB, France
		Inorganic phosphites: original materials for electrochemical storage	Zineb Edfouf, Univ. Rabat, Maroc
17:30	17:40	Farewell messages	Fermin Cuevas

In situ studies of phase-structural transformations in hydrogen and energy storage materials: an overview

Volodymyr A. Yartys

Institute for Energy Technology, Kjeller, Norway

In situ synchrotron X-Ray diffraction and neutron powder diffraction are very useful tools in probing the behaviours of hydrogen storage and battery electrode materials, as allowing to assess the mechanism and kinetics of the transformations in metal hydrides and to determine the atomic structure of the hydrogen-containing materials.

A very significant research attention has been recently allocated to the theoretical and experimental studies of Mg-containing hydrogen storage materials, not only because of the high H storage capacity of magnesium hydride, but also due of the high cost efficiency of use of the abundant Mg alloys/composites and their hydrides. The chemistry and metallurgy of magnesium-containing H storage materials is rather challenging as Mg is prone to easy evaporation and oxidation during the alloys preparation, it shows high rates of corrosion in electrolyte solutions in the Ni-MH batteries, and it causes a significant destabilisation of the metal hydrides creating difficulties in the initiation of the hydrogenation process and increasing hysteresis between the hydrogen absorption and desorption. Thus, operando studies of the Mg-containing materials during their synthesis and during their operation as H storage and battery electrode materials are important to achieve their optimisation. Results of the *in situ* studies at variable conditions as related to the type of the studied Mg-containing materials will be reviewed and include:

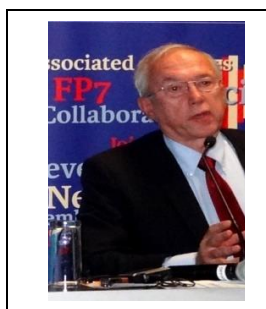
- Temperature-dependent transformations in the RE-Mg-Ni alloys at T up to 1050 °C;
- Studies of the RE-Mg-Ni-D₂ systems at pressures up to 1000 bar D₂;
- Electrochemical charge-discharge processes in the RE-Mg-Ni based anodes of the Ni-MH batteries.
- MgNi₂-D₂ and MgCo₂-D₂ systems at kBar D₂ pressures: structure and HDDR processes.

The effects of nanostructuring of Mg-based compounds/related composites will be considered with a focus on the collaboration with Dr. Michel Latroche [1-3].

[1] Michel Latroche, et al.// *J. Phys. Chem. C*, **2014**, 118 (23), 12162. doi:10.1021/jp503226r.

[2] I.E.Gabis, M.Latroche, et al.// *Electr. Acta*, **147** (2014) 73. doi:[10.1016/j.electacta.2014.08.107](https://doi.org/10.1016/j.electacta.2014.08.107).

[3] V.A. Yartys, M. Latroche, et al. // *Acta Mater.* **98** (2015) 416. doi:[10.1016/j.actamat.2015.07.053](https://doi.org/10.1016/j.actamat.2015.07.053).



Volodymyr A. Yartys

I've got a privilege and a pleasure of having Michel Latroche as a close friend and a scientific colleague and collaborator. Our collaboration lasted for more than two decades and resulted in joint international projects and in 15 common publications (3 papers collected 100+ citations each) focusing on the studies of the rechargeable batteries and on establishing structure-properties interrelation in the metal hydrides and their applications as anodes of the metal hydride batteries and as efficient hydrogen storage materials.

The duality solid-state chemistry / application

Professor Jean-Louis BOBET

ICMCB – CNRS, University of Bordeaux, UPR 9048, F-33600 Pessac, France

The search of new ternary (RE-T-Mg; RE = Rare earth, T = Transition metal) magnesium rich intermetallic candidates for hydrogen storage is of great interest. Four new compounds have been discovered up to now: LaCuMg₈, Gd₁₃Ni₉Mg₇₈, NdNiMg₅ and NdNiMg₁₅. LaCuMg₈ crystallizes in the La₂Mg₁₇ structure type, the Mg atoms form hexagonal tubes along the c-axis filled by La and Mg. For Gd₁₃Ni₉Mg₇₈ the structure was partially deduced using TEM and a modulation along both a* and b* axis was observed. NdNiMg₅ crystallizes within a new structural type with a close-packed array of Mg-atoms. NdNiMg₁₅ crystallizes with a new ternary ordered variant of the V₁₅Sb₁₈ structural type. To our knowledge, among the ordered Mg-rich phases, this new compound is the richest one. In the 3D network of Mg-atoms the Ni and Nd atoms form linear chains. The preliminary studies of its magnetic properties will be presented.

All the compounds presented in the first part decomposed under hydrogen. Nevertheless, in some case, the kinetics are better than those of ball milled magnesium which is rather unexpected. Some other properties such as mechanical ones will also be shortly discussed. Generation of hydrogen from hydrides by the hydrolysis method will be shown. Hydrogen generated from Mg-H hydrolysis reaction was connected directly to a single polymer electrolyte membrane fuel cell (PEMFC). At 0.15 A, the cell voltage exhibited a stable value of approximately 0.52 V for roughly 35 min.



Jean-Louis BOBET

I had the pleasure of meeting Michel more than 20 years ago now at an international conference on Hydrogen. I immediately appreciated his availability and open-mindedness. We have since had many opportunities to see each other and get to know each other a little more. His kindness and good mood were contagious. In his field of research, he was internationally recognized and yet he remained humble and very accessible, especially for all the young students to whom he gave many very useful advices.

We have talked many times about our respective families. We both had 2 daughters that we were very proud of and I can't remember not speaking at each of our meetings over the past 20 years.

His human qualities were like his scientific qualities: exceptional!

Thanks Michel.

New Mg²⁺ ionic conductors in the Mg(BH₄)₂-Mg(NH₂)₂ phases diagram

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^b Institut Charles Gerhardt (ICG), Université de Montpellier, UMR5253 CNRS, ENSCM, Montpellier 34095, France

In a similar manner as the exploration of the LiBH₄-LiNH₂ phases diagram revealing the existence of different Li-B-N-H phases able to release large amounts of hydrogen at moderated temperatures (> 10 wt.% at 250°C for the Li₃BN₂H₈ composition), we have investigated the Mg(BH₄)₂-Mg(NH₂)₂ system. The only compound reported so far in the literature was MgBH₄NH₂, for which a noticeable Mg²⁺ ionic conductivity was measured (1x10⁻⁶ S/cm at 150°C) [1], whereas Mg²⁺ conductivity in the solid state is usually very limited due to the strong polarising nature of the Mg²⁺ cation.

Our work was targeting a systematic exploration of the Mg(BH₄)₂-Mg(NH₂)₂ phases diagram. Different (1-x) Mg(BH₄)₂ + x Mg(NH₂)₂ compositions were ball-milled and, then, annealed. Three new compounds have been identified, labelled α, β and γ, respectively. The α phase with x = 0.75 has the same crystal structure as Mg(NH₂)₂, but a larger unit cell due to the partial (NH₂⁻) substitution by (BH₄⁻) and a higher Mg²⁺ ionic conductivity. For x = 0.67, a new β phase with Mg₃B₂N₄H₁₆ composition is interesting for hydrogen release: 9.6 wt.% of hydrogen are desorbed under vacuum between 200 and 250°C, without significant NH₃ contamination. And, finally, on the (BH₄)-rich side of the phases diagram, a new γ phase with Mg₃B₄N₂H₂₀ stoichiometry (x = 0.33), thermally stable up to 250°C, shows a high Mg²⁺ ionic conductivity of 4.1x10⁻⁵ S/cm at 100°C [2], making this compound one of the solid materials with the highest Mg²⁺ conductivity. During the talk, the possible use of these Mg²⁺ ionic conductors as solid electrolyte for Mg-ion batteries will be discussed.

[1] R. Le Ruyet, R. Berthelot, E. Salager, P. Florian, B. Fleutot, R. Janot, J. Phys. Chem. C, 123 (2019) 10756.

[2] R. Le Ruyet, B. Fleutot, R. Berthelot, Y. Benabed, G. Hautier, Y. Filinchuk, R. Janot, ACS Applied Energy Mater., 3 (2020) 6093.



Raphaël JANOT

I did a post-doctorate under the supervision of Michel Latroche in 2004. I was hired by CNRS in 2005, but kept contact with Michel since then discussing about metal hydrides for hydrogen storage, but also for battery applications. We met frequently, especially during the various annual meetings (GDR ActHyf and HYPAC) organized by Michel. It was also a great pleasure to talk with him at international conferences such as MH and GRC.

Plastic crystals built from (carba -) boron clusters Lego - Excellent solid - state electrolytes

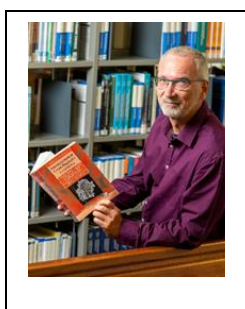
Radovan Černý

Laboratory of Crystallography, DQMP, University of Geneva, Switzerland

Sodium salts of large-cage hydridoborates $[B_xH_x]^{2-}$ ($x = 10,12$), and their C-derivatives $[CB_{x-1}H_x]^-$ have proven to be promising Na-based solid-state electrolytes. Indeed, they show an excellent electrochemical stability, arising from the strong electron delocalization on the anion cluster, as well as low area resistance, low density and soft mechanical properties [1]. Fast cationic motion generally occurs after a polymorphic transition towards higher-symmetry phases. This order-disorder phase transition provides structures with more free sites for the cations, improved conduction pathways as well as an increased rotational energy of the anion cages, which enhances the cation motion. However, such phase change occurs usually above room temperature (*rt*), thus hampering practical applications. Lowering (or suppressing) the phase transition has been made possible by chemical tuning (anion substitution) or physical treatments implying either the formation of composites, nanoconfined materials or by mixing anionic (or neutral) hydridoborate clusters [2-4]. Following this approach, we discovered $Na_4(CB_{11}H_{12})_2(B_{12}H_{12})$ featuring a superior ionic conductivity of 2 mS cm^{-1} at *rt*, with a low activation energy of 314 meV [3]. Electrochemical stability of 4.1 V vs. Na^+/Na is compatible with high-voltage operating positive electrodes.

Recently, we have shown an effect of mechanical milling in stabilizing at *rt* the superionic conductive phase of a single-anion material, $NaCB_{11}H_{12}$ [5]. The high-energy ball milling quenches the metastable, body-centred cubic (*bcc*) polymorph, which exhibits a large number of available Na^+ sites. Macroscopically, this results in a conductivity of 4 mS cm^{-1} at 20°C , without altering the electrochemical stability. Preliminary electrochemical tests show that *bcc*- $NaCB_{11}H_{12}$ withstand a critical current density of 0.12 mA cm^{-2} .

- [1] R. Černý *et al.*, *Chemistry* (Easton). **2020**, 2, 805
- [2] M. Brighi *et al.*, *Cell Press Phys Sci.* **2020**, 1, 100217
- [3] M. Brighi *et al.*, *J. Power Sources.* **2018**, 404, 7
- [4] L. Duchêne *et al.*, *Chem. Commun.* **2017**, 53, 4195.
- [5] F. Murgia *et al.*, *Appl. Materials Interfaces.* **2021**, 13, 61346



Radovan Černý

We had with Michel few things in common: crystallography, interest in metal hydrides and sailing. Both of us were convinced that the crystal structures is at the origin of many important material properties. Both of us moved from hydrogen storage in metal hydrides to use of these materials in electrical batteries. In addition, we became sailors, Michel the true one, educated by the sea in Brittany. We planned but missed our common sailing. Bon vent, Michel!

Crystal Chemistry of Li_3PS_4 and Na_3PS_4 , solid electrolytes for batteries

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S. Islam^c, P. Canepa^d, M. D. Braidia^b, T. Le Mercier^b, H. Bouyanfif

^a LRCS, UMR CNRS 7314, Université de Picardie Jules Verne, Amiens, France

^b SOLVAY R & I, Aubervilliers, France

^c University of Bath, UK

^d National University of Singapore

^e CELLS-ALBA Synchrotron, Barcelona, Spain

^f CNRS, CEMHTI UPR 3079, Université d'Orléans, France

^g LPMC, Université de Picardie Jules Verne, Amiens, France

Solid electrolytes are crucial for next-generation solid-state batteries and immense activity is going on worldwide [1] on many structural families of interest, including the ionic conductors Na_3PS_4 and Li_3PS_4 .

Li_3PS_4 is an attractive solid-electrolyte material that possesses high RT ionic conductivity ($10^{-4} \text{ S.cm}^{-1}$) but the effects of specific synthesis parameters on the material's local structure and transport properties still demand clarifications. Mechanochemistry induces the formation of a variety of $\text{P}_x\text{S}_y^{a-}$ moieties that strongly influence the global transport properties of Li_3PS_4 [2-3].

Na_3PS_4 is another very interesting material with complex crystal chemistry that we will present. The effects of mechanochemical synthesis that lead to increased ionic conductivity in an archetypical sodium ion conductor Na_3PS_4 were not fully understood and we undertook comprehensive analysis based on diffraction (Bragg and pair distribution function), spectroscopy (impedance, Raman, NMR and INS), and ab initio simulations [4-5].

[1] T. Famprikis et al. *Nature Materials*, 18 (12), 1278-1291 (2019)

[2] Ö. U. Kudu et al. *Energy Storage Materials*, 44, 168-179 (2022)

[3] Ö. U. Kudu et al., *J. Power Sources*, 407, pp. 31-43 (2018)

[4] T. Famprikis et al., *Chemistry of Materials*, 33(14), 5652-5667 (2021)

[5] T. Famprikis et al., *J. Amer. Chem. Soc.*, 142(43), 18422-18436 (2020)



Christian Masquelier

I met Michel in so many national & international conferences and workshops at large scale facilities as we had the common taste of undertaking complex structural studies on materials for energy, in particular *operando* during various chemical / electrochemical processes. We loose such a kind man and fine scientist who showed such a bright example to many young scientists and served the community beautifully.

Applications for metal hydrides - current projects and challenges

C. Pistidda¹, P. Jerabek¹, J. Puszkiel³, Y. Shang¹, H. Cao², E. Alvares¹, M. Passing¹, K. Taube¹, J. Jepsen^{1,3}, M. Dornheim¹, T. Klassen^{1,3}

¹ Helmholtz-Zentrum hereon GmbH, Geesthacht, Germany

² Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China

³ Helmut-Schmidt-University / University of the Armed Forces, Hamburg, Germany

This talk describes results from ongoing projects at Hereon, which focus on the development of hydrogen storage materials and storage solutions for mobile and stationary applications as well as on hydrogen compression. The talk will give insights into the developments going on in the H2HybridTank (mobile), HyReflexS and Digi-HyPro projects (stationary and sector coupling).

The experimental work is accompanied by suitable modelling and simulation over various length scales from the atom to the complete storage tank and its integration into different applications. It ranges from atomistic and phase field modelling to support materials development over component simulation by FEM methods including models for storage materials thermodynamics and reaction kinetics to simulation of tank system integration by process simulation. [1]

Furthermore, with respect to the status of supply chains of raw materials which are critical for all materials-based energy storage technologies, recent results for using recycled raw materials for the synthesis of metal hydrides are presented [2 - 4].

[1] E. Alvares et al., CALPHAD (2022), DOI: 10.1016/j.calphad.2022.1024

[2] M. Passing et al., Journal of Magnesium and Alloys, (2022), DOI: 10.1016/j.jma.2021.12.005

[3] Y. Shang et al., Green Chemistry, (2022), DOI: 10.1039/D1GC04709D

[4] Cao H. et al., Sustainable Energy and Fuels, 4 (2020) 1915–1923, DOI: 10.1039/C9SE01284B.



Dr. Klaus Taube

I knew Michel from several joint European projects where I had the pleasure to collaborate with him. I was always impressed by his deep and comprehensive expertise in metal hydrides and beyond. The more, I got to know him as a very friendly, pleasant and open-minded person, and always enjoyed the joint project meetings. The last one took place in Geesthacht in early December 2021. I am truly sorry that we will never have a chance to meet again.

Hydrogen storage properties of Mg-Ni alloys proceed by fast forging

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¹Université Grenoble Alpes, CNRS, Institut Néel, 38000 Grenoble, France

²Laboratoire d'étude des Microstructures et de Mécanique des Matériaux, Université de Lorraine, CNRS, Arts et Métiers ParisTech, LEM3, F-57000 Metz, France

Fast forging is an effective method for inducing severe plastic deformation and promoting hydrogen sorption. Applied to compacts made of Mg and Ni powders, it shows that both activation (first hydrogenation) and desorption kinetics are strongly dependent on the forging conditions, through the induced microstructures and textures. The process applied at room temperature after annealing close to the Mg-Ni eutectic temperature combines the benefit of forging below the brittle-ductile transition (225-250°C) which leads to faster hydrogen uptake during the first absorption due to a more textured fibre along the c-axis and internal stresses that favour hydrogen diffusion through the bulk material, with the preliminary formation of Mg₂Ni during annealing, which favours faster desorption kinetics.

In situ experiments were carried out by neutron diffraction to analyse the mechanisms involved in these reactions. Several cycles were applied in the same conditions. During the first absorption, the rapid formation of Mg₂NiD_{0.3} is followed by the simultaneous formation of the MgD₂ and Mg₂NiD₄. On the other hand, the following absorptions take place in two distinct steps, with first the rapid formation of MgD₂, then the slower formation of Mg₂NiD₄. Moreover, the formation of MgD₂ stops as soon as Mg₂NiD₄ appears. The reaction mechanisms involved at each stage have been identified with respect to the classical models associated with solid-gas reactions. The formation of MgD₂ is associated with a nucleation-growth mechanism at the first uptake, followed by a diffusion-controlled mechanism at subsequent uptakes.

The forging process can be considered a simple, safe and cost effective process for producing large quantities of Mg-based alloys for hydrogen storage. It could replace the highly efficient but energy and time consuming ball milling process, which leads to pyrophoric powders.

[1] J. Wen, P. de Rango, N. Allain, L. Laversenne, T. Grosdidier, J. of Power Sources 480 (2020) 228823.



Patricia de Rango

I especially met Michel these last years during the IEA meetings where we were often the only two French people, and where we had the opportunity to spend good moments, from Death Valley in 2010 to Israel in October 2019, passing by Australia and many other countries...
Michel will leave a great void at ICMPE, but also in the whole metal hydrides community, and far beyond...

HyCARE: we care about hydrogen!

E.M.Dematteis^a, J.Barale^a, M.Costamagna^a, P.Rizzi^a, M.Baricco^a,

^a Department of Chemistry, Inter-departmental Center Nanostructured Interfaces and Surfaces (NIS), and INSTM, University of Turin, Via Pietro Giuria 7, 10125 Torino, Italy

Hydrogen storage technologies allow storing large amounts of energy with elevated energy density in a sustainable way. The optimal hydrogen cycle involves the production from electrical renewable sources by means of water electrolysis, the storage in the most suitable form, and the re-conversion into electrical energy, through a fuel cell. However, the efficient storage of relevant amounts of hydrogen remains a challenge.

Room-temperature forming hydrides, such as TiFe-type alloys, which can absorb and desorb hydrogen at relatively low temperature (below 100 °C) and gas pressure (below 10 MPa), are suitable for large-scale hydrogen storage.[1] The hydrogenation thermodynamics can be tailored by elemental substitution to attain the requested temperature and pressure range of operation.

The HyCARE project (hycare-project.eu) focuses on the improvement of efficiency of energy storage via hydrogen, with a quantity of about 50 kg of stored hydrogen. The project started from the tailoring and optimization of the material composition (TiFe_{0.85}Mn_{0.05}), through a systematic characterization and analyses of the results. In the following, approximately 5 tons of the selected alloy have been produced and characterized. Metal hydride pellets have been placed in low-pressure tanks for large-scale stationary storage, and these have been coupled with a phase change material (PCM) to increase the overall efficiency of the system. The PCM has been selected with a phase transition temperature compatible with the operating conditions of the intermetallic hydride. The storage module will be integrated with an electrolyzer and fuel cells, to close the ideal hydrogen cycle.

[1] Dematteis, E.M.; Berti, N.; Cuevas, F.; Latroche, M.; Baricco, M. Substitutional effects in TiFe for hydrogen storage: a comprehensive review. *Mater. Adv.* 2021, 2, 2524–2560, doi:10.1039/D1MA00101A.

HyCARE project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under Grant Agreement No 826352.



Marcello Baricco

I know Michel from a while: a great scientist, a clever leader, and a good friend.

Hi Michel.
There will be a lot of hydrogen in the heaven: please, store a bit for us.
Ciao, Marcello

Metal tritides aging

S. Challet^a, B. Evin^a, A. Fabre^a, M. Segard^a, S. Thiébaud^a

^a CEA, DAM, Valduc, 21120 Is sur Tille, France

The solid storage in metal hydride is particularly interesting for tritium, a radioactive isotope of hydrogen, as it ensures both safety and compactness. However, the tritium radioactive decay produces helium-3. The generated helium-3 is insoluble in metal and quickly organizes to form nanobubbles that remain trapped in the metal matrix. This phenomenon leads to the aging process of metal tritides which is characterized by the evolution of its physico-chemical properties [1-4].

The study of the metal tritides aging is divided into two parts. The first one is the measurement of physico-chemical properties as a function of aging (PcT curves, swelling, mechanical properties). And the second one is the understanding of the aging mechanisms by the study of the helium-3 bubbles at the microscopic scale [5-8].

- [1] S. Thiébaud et al., Journal of Alloys and Compounds, 356-357 (2003) 36-40.
- [2] S. Thiébaud et al., Journal of Alloys and Compounds, 446-447 (2007) 660-669.
- [3] A. Fabre et al., Journal of Nuclear Materials, 342 (2005) 101-107.
- [4] J.-M. Joubert et al., Journal of Nuclear Materials 395 (2009) 79-88.
- [5] M. Segard et al., Journal of Nuclear Materials, 420 (2012) 388-395.
- [6] B. Evin et al., J. Phys. Chem. C, 125 (2021) 46, 25404.
- [7] M. Segard et al., arXiv, (2021) 2106.01776.
- [8] B. Evin et al., J. Alloys Compd., 878 (2021) 160267.

Sylvain Challet

Personal relationship with Michel Latroche:

Michel has been my PhD director in 2002-2005, a thesis about hydrogen storage for mobile applications.

Since 2009, I lead a collaboration with ICMPE about metal tritides aging, in which Michel was acting as a senior expert.

Enthalpy-entropy compensation in BCC and high entropy alloys

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^a Université du Québec à Trois-Rivières

^b Institut de Chimie de la Matière Condensée de Bordeaux

The relationship between enthalpy and entropy in metal hydrides has been studied. First, a wide composition range of $Ti_{0.63-x}V_xCr_{0.37}$ ($x = 0.3, 0.21, 0.15, 0.12, 0.03$) Body Centred Cubic (BCC) alloys were investigated. In order to facilitate the first hydrogenation (activation), all alloys were melted with 4 wt. % of Zr_7Ni_{10} . All alloys absorbed hydrogen with reversible capacity ranging from 1.5 wt.% to 0.5 wt.%. The enthalpy of formation as well as the entropy changed with alloy's composition. More specifically, both ΔH and ΔS increased as a function of titanium/vanadium atomic ratio. We found that the entropy and enthalpy are in fact linearly correlated showing the so-called enthalpy-entropy compensation effect. This motivated us to investigate another BCC system $Ti_{0.3}V_{0.6}Mn_{0.1-x}$ where $x = 0, 0.033, 0.066$ and 0.1 . A similar enthalpy-entropy compensation was found. Finally, the high entropy alloys of composition $Ti_xHf_{0.25-x}V_{0.25}Zr_{0.25}Nb_{0.25}$ with $x = 0, 0.0625, 0.125 ; 0.1875$ and 0.25 were investigated and showed an enthalpy-entropy compensation. The signification of this relationship will be discussed.

A short history of (hydride-based) batteries

Petra de Jongh

Materials Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University,
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Batteries have been invented more than 200 years ago, but nevertheless still show rapid development and are essential for the energy transition.

In my contribution I will give a very brief overview of the history of batteries, and especially dwell on some of the topics for which the research and inventions of Michel Latroche played an important role, such as the development of nickel metal hydride, alkaline and all-solid state batteries.



Petra de Jongh

The name of Michel Latroche became famous to me when working at Philips, where the nickel metal hydride battery was invented, in the late nineties. The first time I met him was at a conference, and in a very friendly and inviting manner he inquired whether I would not be interested in collaboration. Since then it was a great pleasure to work with him, and regularly come to Paris. His role in the metal hydride and battery community cannot be overestimated. He will be missed.

Use of hydride based materials in all solid state batteries

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For several decades, hydride-based materials were extensively studied for several applications. More particularly, hydride materials are promising candidates to meet the exponentially increasing demand in electrochemical energy storage. They are already used as negative electrodes in nickel-metal hydride batteries for portable or industrial battery applications, such as hybrid electric vehicle or catenary free tramway.

More recently, interest of hydrides in lithium-ion and all solid-state batteries has been demonstrated in high capacity anodes and as a lithium conductive solid electrolyte.

Michel's scientific contribution was very important in all these fields. The presentation will focus on our most recent collaboration activities with Michel's team related to the design of new hydride materials and electrochemistries for solid-state batteries in the frame of the EU funded ECOSTORE project (FP7-ITN-GA-2013-607040).

Christian JORDY

I was PhD student when Michel joined CNRS in Meudon. After my PhD, I continued to work with Michel on many topics in the frame of several collaborations until 2017. During all this time we had very interesting, constructive and fruitful discussions in very friendly atmosphere, which led to several patents and papers. In addition to his high scientific skills, I also appreciated his human qualities.

Metal hydrides as electrolytes for solid state batteries

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Hydrogen has an extremely interesting chemistry and form compounds with most elements in the periodic table and with a variety of different types of bonds. Metal hydrides has recently become very interesting as new classes of energy materials for batteries and hydrogen storage. They are traditionally prepared by mechano-chemistry [1], but now also in combination with solvent-based and solid-gas reactions. This presentation demonstrates that there is still room for discovering new combinations of light elements including boron and hydrogen, leading to complex hydrides with extreme flexibility in composition, structure and properties. Complex hydrides may have structural dynamics in the solid state, i.e. entropy effects, which is important to for fast ionic conductivity in the solid state.

Recently, we discovered a new metal borohydride $\text{Mg}(\text{BH}_4)_2 \cdot \text{NH}_3$ with high Mg^{2+} ionic conductivity. Density functional theory calculations (DFT) reveal that the neutral molecule (NH_3) is exchanged between the lattice and interstitial Mg^{2+} facilitated by a highly flexible structure, mainly owing to a network of di-hydrogen bonds, $\text{N}-\text{H}^{\delta+} \cdots \delta-\text{H}-\text{B}$, and the versatile coordination of the BH_4^- ligand. Di-hydrogen bonds in inorganic matter is a new tool for materials design and have similar bond strengths and bond lengths as hydrogen bonds in biological materials. A composite material $\text{Mg}(\text{BH}_4)_2 \cdot 1.5\text{NH}_3$ is eutectic melting ($\sim 55^\circ\text{C}$) and the melt can be stabilised to form a functional solid material with $\sigma(\text{Mg}^{2+}) \sim 10^{-3} \text{ S cm}^{-1}$ at $T = 70^\circ\text{C}$. We conclude, that the chemistry of hydrides is very divers, towards rational design of multi-functional materials, including new electrolytes for batteries and hydrogen storage materials.

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Torben R. Jensen

I have known Michel Latroche since 2005, where I also became an expert for the International Energy Agency. Here we meet twice per year since then. We were also both partners in a Marie Curie Network for educating 15 young scientist and has together written numerous research proposals. We both shared the same research interests and meet at many research conferences and had many fruitful scientific discussions. We published about 10 scientific papers together, one of those received about 350 citations.

Original Mechanisms observed during Cycling of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ in Na-ion batteries

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Vanadium phosphate positive electrode materials attract great interest in the field of Alkali-ion (Li, Na and K-ion) batteries due to their ability to store several electrons per transition metal. These multi-electron reactions (from V^{2+} to V^{5+}) combined with the high voltage of corresponding redox couples could allow the development of high energy density positive electrode materials for Metal-ion batteries.

For instance, the optimization of the electrochemical performance of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$ required the careful tuning of the oxygen and thus vanadyle-type defects' concentration through a deep understanding and control of the reaction synthesis. Indeed, the competition between the ionic $\text{V}^{3+}-\text{F}$ bond and the covalent $\text{V}^{4+}=\text{O}$ bond has a major effect on the structure of the pristine materials, and then on the phase diagram and redox mechanisms involved upon their cycling in Na-ion batteries. The influence of the anionic substitution will be illustrated combining mainly *operando* Synchrotron X-ray diffraction and spectroscopic studies [1], [2].

Furthermore, unlike the widely believed two-phase reaction in the NASICON $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ - $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ system, a new intermediate $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ phase was identified using *operando* synchrotron X-ray diffraction upon cycling of a battery in non-equilibrium conditions [3]. This intermediate phase reduces the lattice mismatch between $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ phases facilitating a fast phase transition. This work paves the way for a better understanding of great rate capabilities of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$.

Such vanadium phosphates that operate at high voltages are usually unable to reversibly exchange several electrons in a narrow enough voltage range. During this talk, through a short review of redox mechanisms and structural evolutions occurring upon cycling of selected materials, we will identify the crystallographic origin of this trend: the distribution of PO_4 groups around vanadium octahedra, that allows or prevents the formation of the vanadyl distortion ($\text{O}---\text{V}^{4+}=\text{O}$ or $\text{O}---\text{V}^{5+}=\text{O}$) required to stabilize high oxidation state for vanadium [4].

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Laurence Croguennec

J'ai eu la chance de mieux connaître Michel ces dernières années, notamment lors de la construction de l'IRN-FACES avec l'Australie. J'ai évidemment pu mieux apprécier encore ses qualités de scientifique : Michel était un passionné et, pour nous tous, une référence dans le domaine des Matériaux et du Stockage de l'Energie. Mais, j'ai aussi découvert un scientifique chaleureux, bienveillant, et attaché à partager et à transmettre dans la bonne humeur. Merci Michel.



Inorganic phosphites: original materials for electrochemical storage

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In the scope of finding new materials for electrochemical storage, inorganic materials still give a huge area of exploration. In Morocco, we aim the valorisation of natural resources, and as the country has the largest phosphate reserve in the world and phosphate based materials have proven good electrochemical performances, especially LiFePO₄ (LFP) which attracted a great technologic attention as cathode material for lithium-ion batteries, thus, it is necessary to develop a new range of effective materials. Inorganic transition metal based phosphites, for instance, have been fewly studied. Replacing metal phosphates M_x[PO₄]_y (M= metal alkaline and/or transition metal) by metal phosphites M_x[HPO₃]_z is of big interest thanks to the various new structures that can be obtained. In metal phosphate structures, phosphate tetrahedra [PO₄]³⁻ have four connections with the metal. While, phosphite pseudo pyramids [HPO₃]²⁻ have only three connections with the metal making an open framework and larger tunnel structures allowing a better cation diffusion.

In the present work, will be given a global view of our activities in MANAPSE Laboratory concerning original metal phosphite materials which have been discovered and tested as anodes for lithium-ion batteries for the first time by our team. Ti₂(HPO₃)₃ [1,2,3], LiTi(HPO₃)₂ [4] and SnHPO₃ [5,6] compounds will be discussed. These materials were synthesized by simple hydrothermal method and exhibit attractive electrochemical performances.

This class of materials is new and still have to be widely explored. Also, it can be used in different battery components and various electrochemical storage technologies.

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Prof. Zineb EDFOUF

Michel was my co-supervisor with Fermin Cuevas for my PhD thesis at the ICMPE from 2008 to 2011. He was such a second father for me, always present for good advice and quality learning. Helping even for personal matter when needed. Michel called me his spiritual daughter and I appreciated a lot. Michel was engaged in a common PHC Toubkal project with UM5R, which is still in course to encourage scientific collaboration between us. Rest in peace Michel, we love you so much and will continue to carry the flame you lit in us.