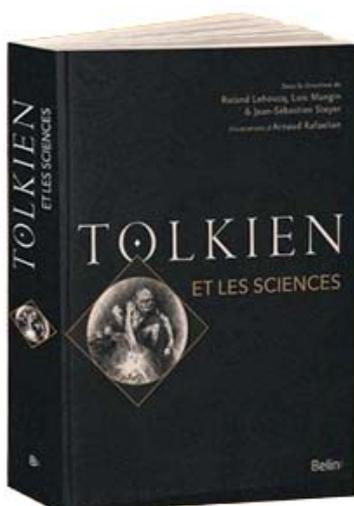


Editorial

The year 2019 has been an eventful one for ICMPE. First, at the institutional level, with the evaluation of our unit by the Hcéres and the globally positive opinion expressed by the visiting committee on our organization and activities during the past five years. This result is to the credit of the staff, permanent and non-permanent, who have committed themselves throughout this mandate to bring our works to the highest level and thus increase the visibility of our actions. Then at the scientific level with notable successes with our funding agencies, including no less than five ANR projects selected in very diverse themes that make the originality of our Institute. Finally, in terms of communication with the organization of numerous events, particularly in the context of the Year of Chemistry, the 80th anniversary of the CNRS and the Ambassadors of Chemistry, but also the participation in conferences or TV broadcasts with a large audience. It is on these tangible successes that our five-year term ends. The ICMPE will continue in 2020 with a new management team to whom we wish lots of accomplishment in the coming years. "The future is not what will happen, but what we will realize" (H. Bergson).

Michel Latroche, Director of ICMPE

Valérie Langlois, Deputy Director



We knew the great writer, creator of worlds, inventor of languages, we discovered J.R.R. Tolkien, the botanist, the paleontologist, the geologist, the archaeology and chemistry enthusiast. In this new collective book "Tolkien and the Sciences", directed by R. Lehoucq, L. Mangin et J.-S. Steyer and published by Belin Editions, no fewer than 39 authors have examined Tolkien's many novels, poems and correspondence to reveal their scientific roots. Among them, J.-M. Joubert and J.-C. Crivello, researchers at the ICMPE, contributed through a chapter devoted to metallurgy in Tolkien's work: Une métallurgie médiévale fantastique.

Sustainable Materials

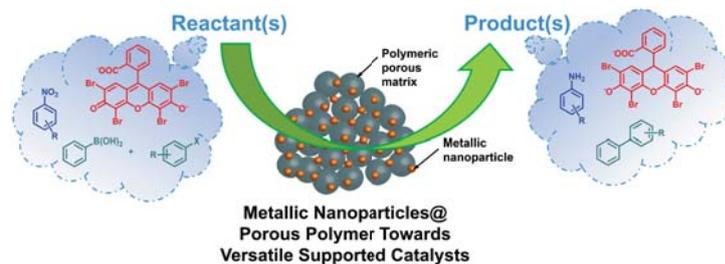
Porous polymers and metallic nanoparticles: A hybrid wedding as a robust method toward efficient supported catalytic systems

This review highlights the original concept relying on the immobilization of metallic nanoparticles at the pore surface of polymeric materials. In such a way, the corresponding hybrid porous materials can act as efficient and sustainable heterogeneous catalysts for a large variety of chemical transformations.

An overview of the main strategies allowing for the preparation of the wide range porous polymeric supports at different porosity scales so far implemented for the immobilization of metallic nanoparticles has been given.

Different crucial parameters regarding the tight immobilization of the nanometal at the pore surface have been pointed out, including the chemical nature of the polymer matrix and that of the metal, the porous morphology of the support as well as the approach used to immobilize the nanoobjects (*in situ* vs. *ex situ*).

Such hybrid materials have been exploited to efficiently catalyze a broad variety of molecular reactions from chemical reduction of nitroaromatic compounds and pollutant dyes to more complex C-C homo and cross-couplings.



R. Poupart, D. Grande, B. Carbonnier, B. Le Droumaguet, *Prog. Polym. Sci.*, 2019, 96, 21-42.

Contact : ledroumaguet@icmpe.cnrs.fr

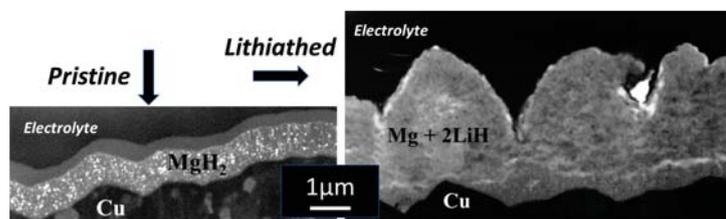


Exploring reversibility issues of the conversion reaction between hydrides and lithium in MgH₂ films

The performances of lithium-ion batteries (LiBs) need to be improved for facing increasing energy demands for stationary and mobile applications. Metal hydrides MH_x, which operate through the conversion reaction: $MH_x + xe^- + xLi^+ \rightleftharpoons M + xLiH$, are promising anode electrode materials for next LiBs generation. They have high mass capacity (above six-fold that of current graphite electrode) and low working potential (below 1V vs. Li⁺/Li). However, they suffer from low reversibility at room temperature.

Thin film of MgH₂ has been investigated for the first time in LiBs to track electrical insulation within the active material as well as eventual mechanical failure during galvanostatic cycling. Transmission electron microscopy combined to electrochemical impedance spectroscopy analyses at different stages of lithiation (see figure below) demonstrate that electronic degradation is not the first cause of irreversibility. Instead, mass-transport limitations within MgH₂ film are pointed out.

This work was undertaken in collaboration with the University of Stuttgart and LPSC/Université Grenoble-Alpes under the EU Marie Curie ITN-ECOSTORE project.



Upon lithiation, MgH₂ film doubles its thickness but no mechanical failure is noticed

N. Berti, E. Hadjixenophontos, F. Cuevas, J. Zhang, A. Lacoste, P. Dubot, G. Schmitz & M. Latroche, *J. Power Sources*, 402 (2018) 99-106.

Contact : cuevas@icmpe.cnrs.fr



γ-Na_{0.96}V₂O₅: A New Competitive Cathode Material for Sodium-Ion Batteries Synthesized by a Soft Chemistry Route

The rising importance of Na-ion batteries (NIBs) in the energy storage solution panel implies to identify novel electrode materials. Here, γ-Na_{0.96}V₂O₅, synthesized by chemical sodiation of the γ'-V₂O₅ polymorph at room temperature, is reported as a new competitive cathode material for NIBs. Thanks to this soft chemistry route, a fine and porous powder with high purity and crystallinity is obtained. The layered structure of γ-Na_{0.96}V₂O₅ allows a quantitative sodium extraction-insertion process at a high voltage of 3.4 V vs Na⁺/Na, with a high reversible capacity of 125 mAh g⁻¹ at C/5 and good cyclability (112 mAh g⁻¹ still available after 50 cycles at C/5, figure 1). These promising electrochemical performances are well explained by the ability of sodium ions to easily diffuse within the interlayer space (figure 2), without causing irreversible structural changes. Indeed, an excellent structural stability upon cycling is probed at long range (XRD) and atomic scale (Raman spectroscopy).

This new sodium vanadium bronze competes with well-known sodium-ion batteries cathode materials such as NaNi_{1/3}Mn_{1/3}Co_{1/3}O₂ and NaFePO₄.

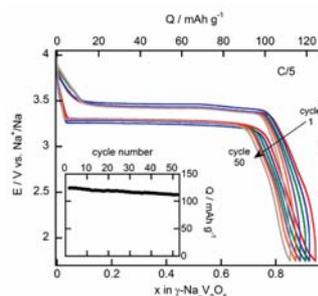


Figure 1: Charge-discharge cycles at a C/5 rate. Inset, specific capacity versus cycles.

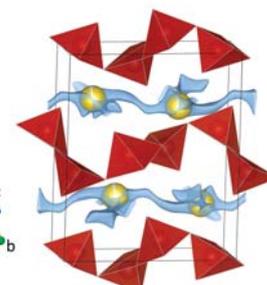


Figure 2: expected sodium diffusion pathway.

N. Emery, R. Baddour-Hadjean, D. Batyrbekuly, B. Laïk, Z. Bakenov, J.-P. Pereira-Ramos, *Chem. Mater.*, 2018, 30, 5305-5314.

Contact : emery@icmpe.cnrs.fr

Past events

- A thematic day of the *Fédération pour l'Enseignement et la Recherche en Métallurgie en Ile de France* (FERMI) was organised at ICMPE by I. Guillot and L. Perrière (ICMPE), Jean-Luc Béchade (CEA) and Mikael Perrut (Onéra) the 14 May 2019, on "[Metals under extreme conditions](#)". The topics were focused on the behaviour of metals under different types of stress (thermal, thermomechanical, corrosive, radiative, and ballistic) in relation to industrial applications.
- The foundations for an Franco-Australian International Research Network (IRN) on *Energy conversion and storage for autonomous and maritime applications* were laid during the [first "IRN-FACES" workshop organized by ICMPE and the University of New South Wales at Croisic \(France\) on 13-14 June 2019](#), with 40 participants (11 Australians) and supported by Naval Group, Engie and PadoTech. The network consists of 8 CNRS laboratories (ICMPE, ICMCB, IEM, IMN, IMS, Ampère, LAPLACE and Femto-ST) and four Australian universities (UNSW, Deakin, Flinders and UNiSA). It has been approved by CNRS and will be launched in January 2020.
- [The 5^e Journées de la Société Française des Semiconducteurs et Oxydes Poreux \(SCOPE\)](#) took place at ICMPE (S. Bastide) on 19-20 June 2019 and brought together some thirty French and European researchers.
- The first Annual Days of the GDR "High Entropy Alloys" were held in Nantes (IMN) on 25 and 26 June



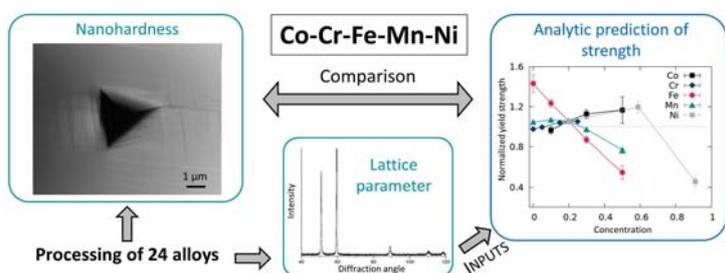


Combining experiments and modelling to explore the solid solution strengthening of high and medium entropy alloys

In a context of always more demanding structural applications, there is a need to create new families of metallic alloys. High entropy alloys, which are multi-component and single-phase, are meant to widely explore chemical compositions which should allow to. This is both a huge opportunity for discovering alloys with unprecedented properties. This is also a challenge to be able to do so in a reasonable amount of time. In this context, we defined an exploring strategy which combines:

- a simplified metallurgical processing, followed with structural characterization and mechanical testing by nanoindentation. Thus a large number of compositions from the Co-Cr-Fe-Mn-Ni system were experimentally tested.
- an analytical modelling of solid solution strengthening with no adjustable parameters.

First, a good quantitative agreement was proven between experiments and modelling. Second, new compositions with improved mechanical properties were identified. This study opens the perspective of a complete description of the quinary system and of a multi-properties optimization.



G. Bracq, M. Laurent-Brocq, C. Varvenne, L. Perrière, W.A. Curtin, J.M. Joubert, I. Guillot. *Acta Mater.* 177 (2019) 266-279.

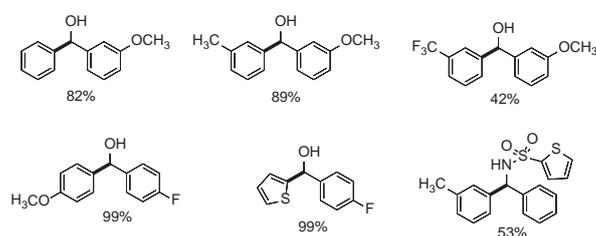
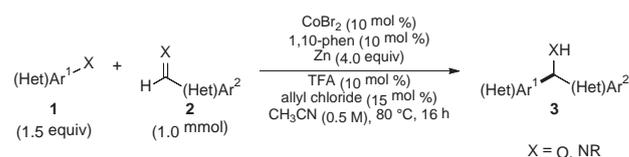
Contact : laurent-brocq@icmpe.cnrs.fr



Co^I-Catalyzed Barbier Reactions of Aromatic Halides with Aromatic Aldehydes and Imines

The addition of organometallic reagents to carbonyl compounds is one of the most fundamental C-C bond-forming reactions, which is described in all standard textbooks. However, this approach suffers from two well-known drawbacks: it usually requires the pre-formation of the requisite organometallic reagent and remains limited to substrates without sensitive functional groups. Among the numerous progresses made in the field, the elaboration of reductive cross-coupling reactions between two electrophiles has recently received a considerable attention.

In this article, we describe the reductive Barbier coupling of aromatic halides and electrophiles using a CoBr₂/1,10-phenanthroline catalytic system and overstoichiometric amounts of zinc. The reaction displays a broad scope of substrates (*cf.* scheme below), including (hetero)aryl chlorides as pro-nucleophiles and aldehydes or imines as electrophiles, leading to diarylmethanols and diarylmethylamines in moderate to excellent yields, respectively.



M. Presset, J. Paul, G. N. Cherif, N. Ratnam, N. Laloi, E. Léonel, C. Gosmini, E. Le Gall, *Chem. Eur. J.*, 2019, 25, 4491-4495

Contacts : presset@icmpe.cnrs.fr; legall@icmpe.cnrs.fr

2019, with a scientific and technical symposium on high entropy alloys and complex concentrated alloys, followed by the first GDR General Assembly. They were organized by A. Fraczkiewicz (École des Mines, St-Etienne), F. Tancret (IMN) et I. Guillot (ICMPE).

• The XVIth triennial International Conference "Intergranular and Interphase Boundaries in Materials" took place from 1 to 5 July 2019 at the École de Chimie de Paris (CPT-PSL). It was organized by S. Lartigue-Korinek (MCMC-ICMPE) and O. Hardouin Duparc (LSI, École Polytechnique). Topics covered: Structure and properties of grain boundaries and heterophase interfaces.



• As part of the CNRS' 80th anniversary celebrations, [the History of Rare Earths was presented on 3 October 2019 at ICMPE](#) (co-organizer: V. Paul-Boncour), with a focus on French excellence in this field. The applications of RE in modern materials have been described in their various aspects: permanent magnets, lasers, catalysts, batteries, superconductors. The prospective aspects around rare earths were also addressed with the questions of supply, recycling or their replacement.

• ICMPE had the honour to welcome Professor Ulrich Wiesner from Cornell University (USA) on 14 October 2019, as part of the "Ambassador of Chemistry" action launched by INC on the occasion of the 80th anniversary of CNRS. Prof. Wiesner gave a seminar on the "Convergence of Soft and Hard Condensed Matter Science".



Distinctions

The academic palms were awarded to Jacques Moscovici, UPEC-ICMPE senior lecturer and dean of the UPEC Faculty of Sciences since 2013, on the occasion of the Faculty's New Year's greetings the 24th of January 2019.

Welcoming our new staff members

Hélène Bernard Barrès is the new Administrative director of ICMPE since June 2019. Hélène has been working for CNRS since 1994; she was HR and Training Manager and later on affiliate Professor at Grenoble Graduate School of Business in HRM & intercultural Management. She is graduate from Grenoble Ecole de Management and has completed a Master in Strategic Human Resource Management in England (University of Newcastle, 1992).



ICMPE acknowledges contributions of its members in writing books, chapters and review articles

- Book on the *Chimie des solutions* by Marc Blétry and Marc Presset, which presents the techniques for determining equilibria in a unified way, from usual approximations to numerical calculations, [Ed. de Boeck Supérieur](#).
- Book chapter by Loïc Perrière, in collaboration with Yannick Champion (SIMAP) and Frédéric Bernard (Uni. de Bourgogne) on the *Spark Plasma Sintering of Metallic Glasses*, in [Spark Plasma Sintering of Materials - Advances in processing and applications](#), dir. P. Cavaliere, Springer.
- A *Comprehensive review on electrospinning techniques as versatile approaches toward antimicrobial biopolymeric composite fibers* by H. Rodríguez-Tobías, G. Morales, D. Grande, [Materials Science and Engineering C, 2019, 101, 306](#).
- A review by Michel Latroche, Fermín Cuevas and co-authors on *Full-cell hydride-based solid-state Li batteries for energy storage*, [Int. J. Hydrogen Energy, 2019, 44, 7875](#).
- A review on the Interactions of Hydrogen with Pd@MOF Composites by A. Malouche, C. Zlotea and P. Á. Szilágyi, in [ChemPhysChem 2019, 20, 1](#).
- Contributory chapter *Une métallurgie médiévale fantastique* by J.-M. Joubert and J.-C. Crivello to the Book "*Tolkien et les sciences*" directed by R. Lehoucq, L. Mangin et J.-S. Steyer and published by [Belin Editions. ISBN 978-2410000757](#).

Scientific communication

- Michel Latroche, ICMPE's Director and expert of the Int. Energy Agency, has authored an editorial article published in partnership by "Le journal du CNRS" and daily newspaper Libération on Rare Earths and their future: "*For reasons that have little to do with their abundance, the problems linked to the supply of what are known as "rare" earths could slow the environmental transition. Chemistry can offer some solutions*". [Libération, CNRS Le Journal, 9/5/2019](#).
- The CNRS Institute of Chemistry (INC) has designed a national training day for secondary school teachers to enrich their knowledge in chemistry. [ICMPE was chosen to organize this event for the Académie de Créteil](#), which took place on April 3, 2019 in the presence of 80 teachers.

A presentation on advances in chemistry in the fields of energy, materials, environment and health was given by M. Latroche and



a thematic conference on "Calculation, modelling, artificial intelligence... in support of solid-state chemistry" by J.-C. Crivello (CMTR). Workshops focused on scientific experiments and instruments were also organized in the various ICMPE's teams.

- TF1 journalists requested ICMPE's expertise for a report entitled: "Pollution: the plague of throwing scooters (*trottinettes*) into the water". F. Cuevas (CMTR), provided information on the chemical composition of Li-ion batteries and their dangerousness in water environment during this report broadcast during the 8 pm news of October 16.



ANR Projects 2019

- *Photo-assisted production of hydrogen urea oxidation (Hyurea)*, coordinated by C. Cachet-Vivier (ICMPE), with LISE (Paris), LGE (Toulouse) and SIAAP (Colombes).
- *Multi-principal-element Alloys as Solid Stores for Hydrogen (MASSHY)*, coordinated by C. Zlotea (ICMPE) with Institut Néel (Grenoble), University of Uppsala (Sweden).
- *Development and characterization of new oxygen-tolerant titanium alloys (TITOL)*, involving I. Guillot and J.-P. Couzinié (ICMPE), IRCP (Paris), CES, Soleil Synchrotron (Gif/Yvette) and CEA.
- *Development of carbon monoxide-Releasing Molecules conjugated to polysaccharide carriers targeting adipose tissue for the treatment of obesity (SWEET-CO)*, involving M. Rivard (ICMPE) and IMRB (Créteil).
- *Microbial Alteration and preservation of Monuments in urban area (MIAM)*, involving D.-L. Versace (ICMPE), LEESU (Créteil) and LISA (Créteil).

Up-coming workshops and conferences

- ICMPE will host the 10th workshop *Batteries Lithium en Île-de-France*, organized by R. Baddour-Hadjean, J.-P. Pereira-Ramos and G. Bernari, (ICMPE-GESMAT) and H. Groult (Sorbonne Université) the 12th of Dec. 2019 at ICMPE. Free inscription. Contact: bernari@icmpe.cnrs.fr
- A FERMI thematic day on *The contribution of transmission electron microscopy to metallurgical studies*, organized by Ivan Guillot (ICMPE), will take place at Chimie Paris on 13 December 2019. This day will mark the inauguration of the new transmission microscope installed at ENSCP.
- ICMPE is organizing a one-day conference on Alkaline Earth Materials on 15 November 2019, with presentations by researchers from the institute and the participation of the start-up Adionics.
- A Franco-German workshop on thermodynamics will be held at ICMPE (J.-M. Joubert) on Nov. 21-22/2019, bringing together more than 50 members of the GdR TherMatHT and Deutsche Gesellschaft für Materialkunde (DGM). Communications will cover experimental/computational determination of thermodynamic quantities, Calphad modeling methods and applications on a large number of inorganic systems (metallic, ceramic, glass...).
- The GDR High Entropy Alloy will be organized at ICMPE from June 15 to 17 by the MCMC team. The first day (15/6) will be dedicated to simulation/modeling/Thermocalc for HEA.

ICMPE News

Publisher : Michel Latroche
Coordination : Stéphane Bastide
Mise en page et Impression : Nicolas Boisseau

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