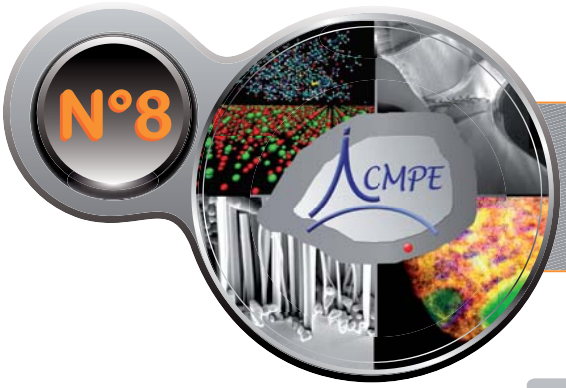


News

International Newsletter

January 2017

Editorial

During the year 2016, our Institute continued to develop its fundamental research in various scientific fields. For this eighth edition of our newsletter, we wish to shed light on five papers covering a broad overview of our activities, from metallurgy to polymers, from energy storage to advanced materials and biomaterials. These cutting edge activities are primarily devoted to basic science but are never disconnected from applications because science must also support innovation.

Fortunately, we can count on two new young scientists recruited this year, an assistant professor of UPEC and a researcher of CNRS. No doubt that this fresh blood will drain innovative research in our laboratories and we wish them a successful career at ICMPE.

In addition to science, our researchers also participate actively in scientific dissemination, organize international workshops and congresses, write books and journals, lead international laboratories (LIA) or participate in radio broadcasting. Good science makes sense when communication is at its best.

Finally, we warmly congratulate our staffs who have received awards and honors this year, they are very much involved in the renown of our Institute.

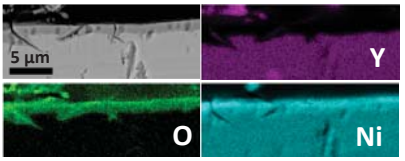
Michel LATROCHE, Director of ICMPE.

Energy Storage

Relationship between H_2 sorption properties and aqueous corrosion mechanisms in A_2Ni_7 hydride forming alloys (A = Y, Gd or Sm)

Metallic hydrides are able to store reversibly hydrogen either chemically and electrochemically near ambient conditions. Thanks to these remarkable sorption properties, those materials has led to the successful development of alkaline Ni*M*H batteries. These technology is used worldwide and, for example, equipped most of the commercial Hybrid Electric Vehicles (HEV) like the Toyota Prius or hydrogen-powered Mirai cars for auxiliary energy storage.

To support these commercial applications, the endless growing needs in term of specific capacities, safety, lifetime and, cost reduction lead to increasing basic research to develop new materials with outstanding properties. Our current works address the development of new families of anode compounds, based on metallic A_2B_7–type hydrides (A = Rare Earths; B = Ni). Influence of rare earth composition on properties of interest such as thermodynamic, cycling stability and corrosion are studied. Electrodes were electrochemically cycled and special attention was paid to calendar and cycling corrosion processes. A mechanism, based on the nature of the corrosion products, has been proposed opening new insights for these promising anode materials.



SEM-EDX mapping of a cross sectional view of Y_2Ni_7 corroded one week.

V. Charbonnier, J. Monnier, J. Zhang, V. Paul-Boncour, S. Joiret, B. Puga, L. Goubault, P. Bernard and M. Latroche, J. Power Sources, 326 (2016) 146-155.

http://dx.doi.org/10.1016/j.jpowsour.2016.06.126

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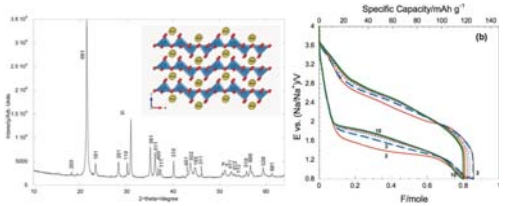
Energy Storage

Electrochemically formed α'-NaV_2O_5: A new sodium intercalation compound

Recently, the concept of sodium-ion batteries has become the most appealing alternative to lithium ion systems for reasons of cost and limited resources of lithium. With a standard electrochemical potential close to that of lithium (-2.71 V/SHE for Na^+/Na instead of -3.04 V/SHE for Li^+/Li), sodium can achieve reasonable tensions with appropriate intercalation materials. Its larger ionic size may however result in a smaller specific capacity than that of lithium and probably slower insertion kinetics.

The insertion of sodium in vanadium pentoxide (V_2O_5) is demonstrated to occur in two distinct steps. A structural study combining X-ray diffraction and Raman microspectrometry shows that the first step corresponds to the irreversible electrochemical formation of the orthorhombic bronze $Na_1V_2O_5$, isomorphic to the high temperature orthorhombic α'-NaV_2O_5 bronze. During the second step, at 1.4 V, a remarkable value of up to 0.8 sodium ions can be reversibly inserted in NaV_2O_5. A very interesting "zero strain" character is evidenced for NaV_2O_5, with only negligible structural changes after Na insertion.

This new electrode material exhibits a stable specific capacity of 120 mAh/g near 1.6V at C/10 rate after 10 cycles at room temperature.



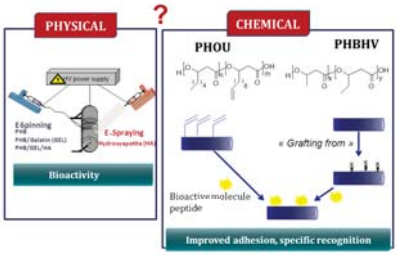
D. Muller-Bouvet, R. Baddour-Hadjean, M. Tanabe, L.T.N. Huynh, M.L.P. Le, J.P. Pereira-Ramos, Electrochimica Acta, 2015, 176 , 586.

Contact : muller@u-pec.fr

Biomaterials

Design of Functionalized Biodegradable PHA-Based Electrospun Scaffolds Meant for Tissue Engineering Applications

Modification of electrospun nanofibrous poly(3hydroxylakanoate) (PHA)-based mats was implemented through two routes to obtain biomimetic scaffolds meant for tissue engineering applications. The first strategy relied on a physical functionalization of scaffolds thanks to an original route which combined both electrospinning and electrospraying, while the second approach implied the chemical modification of fiber surface *via* the introduction of reactive epoxy groups to further conjugate bioactive molecules. Epoxy groups were modified through the attachment of a peptide sequence, such as Arg-Gly-Asp (RGD), to obtain biofunctionalized scaffolds. SEM and TEM analyses of mats showed uniform and well-oriented beadless fibers. The electrospinning/electrospraying tandem process afforded fibers with a surface largely covered by the electrosprayed bioceramic, *i.e.* hydroxyapatite. Gelatin was added to the latter PHA-based scaffolds to improve their biological properties, in particular cell adhesion, proliferation, and osteogenic differentiation. Human mesenchymal stromal cells exhibited a better adhesion and proliferation on the biofunctionalized scaffolds than that on non-functionalized PHA mats.



D. Grande, J. Ramier, D.-L. Versace, E. Renard and V. Langlois, New Biotechnol., 2016, in press
http://dx.doi.org/10.1016/j.nbt.2016.05.006

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Past workshops

- The 7th GFP-IdF workshop on **"Polymères fonctionnels : de la chimie aux propriétés"** was held at ICMPE the 8th of July 2016 (D. Grande).

- **The 3rd edition of the "Journées scientifiques Franco-Maghrébines"** devoted to the characterization of complex materials was organized by UPEC, ENIT and ICMPE at Thiais the 28th-30th of Nov. 2016. They are part of an international scientific cooperation between higher education institutions from south countries and France (2014-Tunisia, 2015-Algeria).

- A **"French-Japanese seminar on green production and storage of hydrogen"**, has been organized at Osaka the 6th of December 2016 by the French Embassy in Japan and the STOPHE Axe led by F. Cuevas (ICMPE) in the frame of the GdR-HySPàC.

Advanced Materials

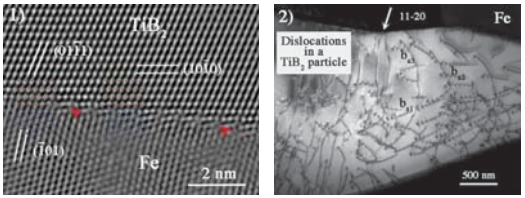
Interfaces and defects in a successfully hot-rolled steel-based composite Fe–TiB_2

The requirement for weight reduction in the automotive industry has led to the development of novel, steel-based composites reinforced with titanium diboride ceramic particles. The product displays a significant increase in stiffness and a low density in comparison with usual steels. It is solidified directly from the melt by eutectic solidification and can be processed through the use of industrial continuous casting devices. The TiB_2 particles are homogeneously distributed. The composite has been successfully hot rolled with a very limited final damage attributed to two main features:

- A good coherency between Fe and TiB_2 phases. At the atomic scale dislocations almost periodically spaced in the iron phase accommodate the residual misfit (in red in figure 1).

- A significant plastic deformation in the TiB_2 particles, with the activation of various slip systems (figure 2). It is interpreted by the presence of metallic Ti-Ti bounds.

All these characteristics may account for the good behaviour of the composite in terms of hot rolling capability.



S. Lartigue-Korinek, M. Walls, N. Haneche, L. Cha, L. Mazerolles and F. Bonnet, Acta Mater., 2015, 98, 297.

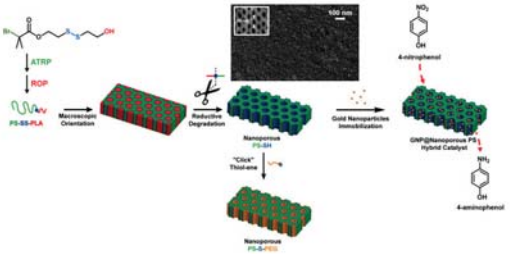
Contact : lartigue@icmpe.cnrs.fr

Advanced Nanomaterials

"Clickable" Thiol-Functionalized Nanoporous Polymers: From their Synthesis to Further Adsorption of Gold Nanoparticles and Subsequent Use as Efficient Catalytic Supports

Thiol-functionalized nanoporous materials could be engineered from novel PS-*b*-PLA diblock copolymers containing a disulfide bridge at the interface between the two distinct blocks. These copolymers were synthesized from a new asymmetric difunctional initiator through controlled polymerization processes. After macroscopic orientation of the precursor copolymers and quantitative reduction of the disulfide bridge in a suitable solvent, well-defined nanoporous materials were obtained. The presence of thiol functions on the pore surface was demonstrated by EDX, and it allowed for further "click" thiol-ene-mediated functionalization of the resulting porous materials with an olefin-bearing model compound, *i.e.* allyl-terminated PEG. More interestingly, thiol-coated nanoporous polymeric frameworks allowed for the robust immobilization of gold nanoparticles at the surface of the nanochannels, and such hybrid systems could efficiently be used as supported catalysts for the reduction of nitro compounds.

This investigation paves the way for further functionalization of thiol-coated porous nanoreactors with interesting model compounds that could find applications in the design of innovative catalytic supports or selective membranes.



B. Le Droumaguet, R. Poupart and D. Grande, Polym. Chem., 2015, 6, 8105.

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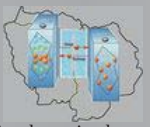
Up-coming workshop



• ICMPE hosted the **7th workshop "Batteries Lithium en Île-de-France"** organized by J.-P. Pereira-Ramos (ICMPE) and H. Groult (PECSA), the 14th of December 2016. The latest results on Li and Na ion batteries have been presented during this meeting.
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See ICMPE on the web for more information

• ICMPE and SIMAP (Grenoble) organize in June 2016 the **46th Calphad meeting in Saint-Malo,** chaired by J.-M. Joubert (CMTR). This international conference will gather 200 researchers from all around the world. It deals with experimental determination of phase diagrams, DFT calculations of phase stability and thermodynamic modelling by the so-called Calphad method of systems useful for materials science.

Distinctions

Dr. Daniel Grande was awarded "Junior Distinguished Member 2015" by the French Chemical Society during a celebration held on May 26th, 2016. This distinction recognizes a young researcher (less than 45 years old) who has achieved a significant progress in one of the fields of chemistry or has demonstrated important actions in chemical education or its dissemination.

Pr. Victor Nikonenko was appointed the 5th of september 2016, by decree of the Prime Minister Manuel Valls (on a proposal of the Ambassador of France in Moscow), the rank of Officer in the National Order of Academic Palms. For this high distinction, the French government recognizes the contribution of Pr. Nikonenko at strengthening the cooperation and scientific exchanges between France and Russia, in particular between ICMPE and the Membrane Institute at the Kuban State University in Krasnodar (MI-KubSU).

Welcoming our new researchers

ICMPE is very pleased to welcome **Dr. Céline Barreteau** as a new permanent CNRS scientist. She graduated from University Pierre et Marie Curie in Paris, received her PhD from University Paris-Sud in Orsay and completed a post-doc at the University of Geneva. She will be working in the "Equipe de Chimie Métallurgique des Terres Rares" (CMTR) on thermoelectric materials.

We are also welcoming **Dr. Agustin Rios de Anda**, Assistant Professor attached to the University Paris-Est Créteil. He obtained his Engineering degree from the National Institute of Applied Sciences in Rouen, then pursued a PhD at the Advanced Polymers and Materials Laboratory in Lyon. He then completed two post-docs at the University of Bayreuth in Germany and at the "Centre de Recherche sur les Macromolecules Végétales" in Grenoble. He will be working in the "Equipe Systèmes Polymères Complexes" focusing on the thermomechanical characterization of polymers.

Science dissemination

Michel Latroche, head of ICMPE (CMTR), spoke at a conference on **"Hydrogen, clean energy for tomorrow"** as part of the "Dialogues - Key to understanding" series of conferences organized by the CNRS and CNAM (June 6 at 6:30 pm) and the same day on RFI during the show "Discussion around the question: What energy vector for tomorrow?" when he was questioned by Caroline Lachowski.

The work of the **SPC team** made headlines in the CNRS Institutes Newsletter (January 2016 edition), under the heading *"**Direct from INC labs: New nanoporous polymers as catalyst supports. How to immobilize metal nanoparticles on a support for optimal catalytic reactions?** Researchers of ICMPE have just developed new porous, inexpensive, flexible and functionalized polymers capable of effectively fixing gold nanoparticles. They thus succeeded in catalyzing the reduction of nitroarenes on several successive cycles with very good yields." These results, published in the journal Polym. Chem. 2015, 6, 8105 (B. Le Droumaguet) are presented in page 3 of this Newsletter.*

ICMPE acknowledges contribution of its members in co-editing book and writing book chapters:

Micro- and Nano-Structured Interpenetrating Polymer Networks: From Design to Applications. S. Thomas, D. Grande, U. Cvelbar, K. V. S. N. Raju, R. Narayan, S. Thomas, H. Akhina, Co-Eds.; John Wiley & Sons: Hoboken, NJ, 2016; including **Chapter 5** "Macro-, meso-, and nano-porous systems designed from IPNs", pp.127-143, by D. Grande.

Crossing porosity scales in functional polymer materials: From design to application. D. Grande, In Polymer Science: Research Advances, Practical Applications, and Educational Aspects; Méndez-Vilas, A., Solano, A., Eds.; Polymer Science Book Series, Formatex Research Center: Badajoz, 2016; pp. 579-591.

Electrospinning and electrospraying techniques for designing antimicrobial polymeric biocomposite mats. H. Rodríguez-Tobías, G. Morales, D. Grande, in Nanofiber Research – Reaching New Heights; Rahman, M. M., Asiri, A. M., Eds.; InTech: Rijeka, 2016; **Chapter 5**, pp. 91-106.

Design of functional nanoporous polymeric materials from self-organized block copolymers. D. Grande, B. Le Droumaguet, In Nanopores and Nanoporous Materials; Morton, T., Ed.; Nova Science Publishers: New York, 2016; **Chapter 1**, pp. 1-26.

ICMPE News

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