N°4

News
International Newsletter

November 2012

Editorial

In the course of 2012, ICMPE has continued to work hard trying to bring its scientific project at its best. Several European research programs have been launched (ITN Marie Curie NANOS3, COST actions, ERANET NOVELMAG, etc) that will strengthen our international relationships. Among the recent events, we can also mentioned our participation to the "Action Nationale de Formation" on Fundamental Metallurgy organised by the CNRS-INC at Aussois, end of October. A special word should be also given about the starting of the LABEX MMCD in partnership with Cermics, MSME and Navier from the PRES Paris Est.

We want to congratulate our youngest but brilliant scientists like Wendy Garcia-Vasquez who got the young scientist second award at the Ion Transport in Organic and Inorganic Membranes Conference held at Tuapse in Russia, last May. Thanks also to Hoda Emami Meybody who obtained the excellent poster award at the MH2012 conference held in Kyoto, Japan this October.

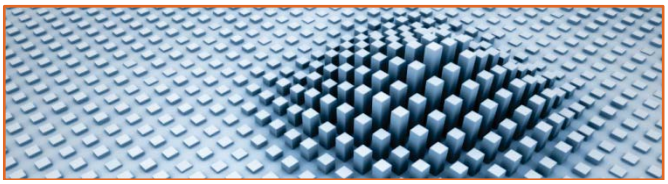
Beside these successes, efforts are still ongoing to improve our efficiency. Several new equipments are foreseen like a new XPS machine and a RF pulverisation device that will reinforce our capacity in the field of surface chemistry. Some reorganisations in our research teams are also on their way and will allow to better rationalize our activities. And last but not least, important refurbishing works are now conducted in two of our main research buildings that will allow working in new and safer chemistry rooms at the end of next year.

All these actions are very important and they demand involvement and patience for most of our personal. We especially want to thank our technical staff for its strong support and high professionalism in the frame of these evolutions. Their help is highly appreciated by all of us in our Institute.

We are now planning next year with confidence and will continue to give our best to build a bright future to ICMPE.

Michel Latroche,
Director of ICMPE

Advanced Materials



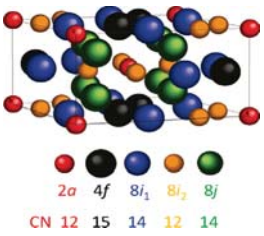
Comparison of the site occupancies determined by combined Rietveld refinement and density functional theory calculations: example of the ternary Mo–Ni–Re σ phase

To improve the high-temperature properties of Ni based super-alloys (used for example in jet engine turbine blades), refractory elements are added. However, they form fragile intermetallic phases. To predict them and prevent their precipitation, models based on the site occupancies of these phases are developed.

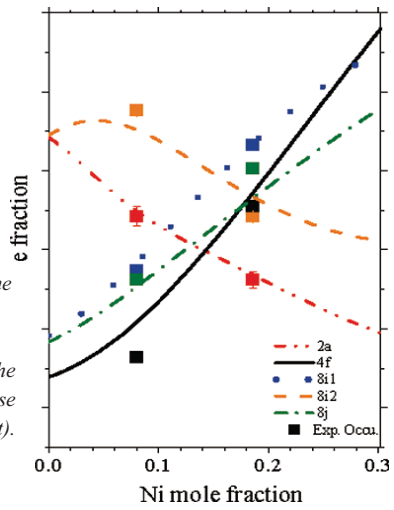
Determining occupation rates of a complex phase in a ternary system is no easy feat, especially for Frank-Kasper intermetallics with 5 non-equivalent crystallographic sites (σ phase).

This article presents the study of the σ phase of the Mo-Ni-Re system, representative of these super-alloys. For the first time, the site occupancies found by the joint refinement of X-ray and neutron diffraction are compared to results calculated *ab initio* by coupling the combinatory energy estimations by DFT and an ideal solution approximation (Bragg-Williams).

The elements of comparison show an excellent agreement between the two sets of results and allow the validation of both the experimental and theoretical approach.



Crystallographic structure of the σ phase.



Re occupancy in the Mo-Ni-Re σ phase (– theory, ■ experiment).

K. Yaqoob, J.-C. Crivello and J.-M. Joubert, Inorganic Chemistry, 2012, 51 (5), 3071-3078

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Solar Energy

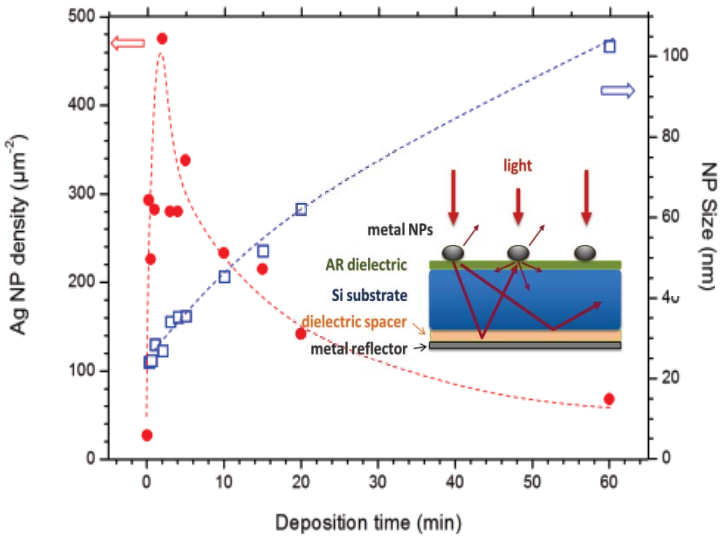
Facile metallization of dielectric coatings for plasmonic solar cells

Plasmonic nano-structures are new promising optical tools for photovoltaic devices. In thin film solar cells, scattering of incident light by metal nanoparticles (NPs) can strongly improve light trapping and absorption, due to their localized surface plasmon resonance (SPR) properties, as schematized in the Figure.

The metal NPs are most commonly deposited through thermal evaporation of metal layers subsequently dewetted by annealing. However, this is cost and time expensive and cannot be applied for large scale device production.

In this article, we report on a new and facile electroless deposition technique for producing Ag NPs on SiNx:H dielectric films used in photovoltaic devices. The driving force is the presence of Si nanoclusters in the dielectric that play the role of sacrificial anode in HF electrolyte for the reduction of Ag ions.

The method allows a good control of the NP density and size, which increases almost linearly with the treatment time (cf. Figure). Its implementation in a solar cell process can take advantage of already existing fabrication steps and equipment and thus could be useful for the realization of various plasmonic solar cell architectures involving dielectrics like SiN_x:H or SiO_x.



S. Bastide, T. Nychyporuk, Z. Zhou, A. Fave, M. Lemiti, Solar Energy Materials and Solar Cells, 2012, 102, 26-30

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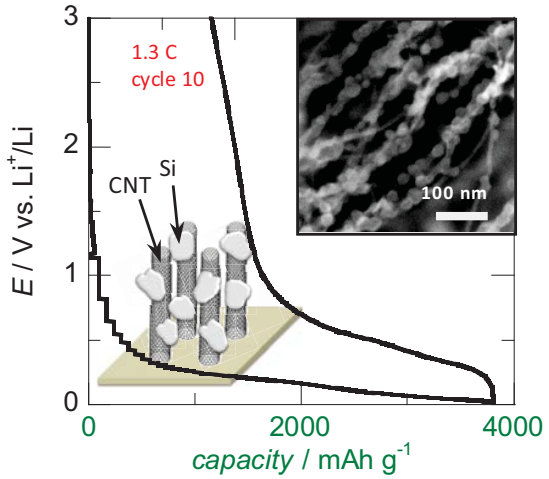
Energy Storage

High-Rate Capability Silicon Decorated Vertically Aligned Carbon Nanotubes for Li-Ion Batteries

Batteries are made of two electrodes separated by the electrolyte. In order to increase battery energy to meet the increasing demand for extended autonomy, the specific capacity and the rate capability of each electrode have to be maximized. In this way, the electrode material can be either changed, or modified, or structured.

In this article devoted to the negative electrode, an original architecture combining vertically aligned carbon nanotubes decorated with dispersed silicon nanoparticles is presented as very promising electrode material.

Indeed, this three-dimensional architecture presents the advantage of using both carbon (excellent contact with the current collector as NTC are directly grown onto ; good electron transport pathway) and silicon (theoritical capacity close to 3600 $mAh.g^{-1}$, 10 times higher than those of commercial carbon ; nanosized particles enabling the accommodation of volume changes during lithiation and delithiation processes). Electrochemical performances show an impressive rate capability: 1900 $mAh.g^{-1}$ at 5 C and 760 $mAh.g^{-1}$ at 15 C and a good cyclability: 800 $mAh.g^{-1}$ are still recovered after 100 cycles at 10 C.



Gohier, A., Laïk, B., Kim, K.H., Maurice, J.L., Cojocaru, C. S., Pereira-Ramos, J. P., Tran Van, P. Advanced Materials 2012, 24(19), 2592–2597, doi : 10.1002/adma.201104923

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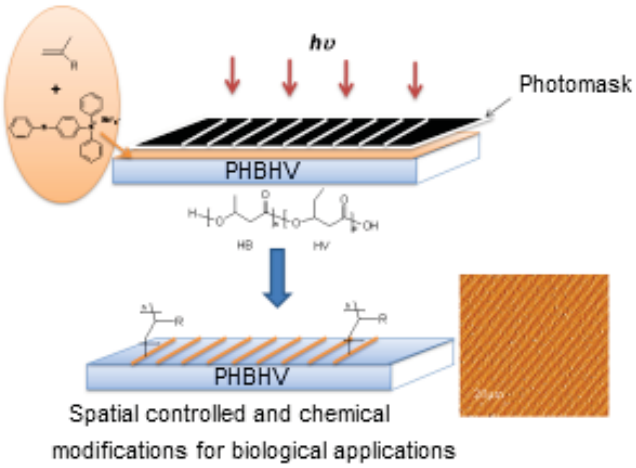
Bio-Resources

Natural biopolymer surface of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) photoinduced modification with triarylsulfonium salts

Due to the global decrease of fossil fuels storage and their rising prices, a renewal of interests towards new monomers derived from renewable resources is observed. This evolution motivates academic and industrial research to develop novel materials labeled as “environmentally-friendly”, *i.e.*, materials produced from alternative resources, biodegradable and non-toxic to the environment.

Poly(3-hydroxyalkanoate) (PHAs) belong to new families of biodegradable and biocompatible polymers of the aliphatic polyester family. They appear as promising materials and have attracted much attention for a variety of medical applications. However, and despite its many attributes, the intrinsic hydrophobic properties of PHAs restrict their applications as cell colonizing materials. As a consequence, the surface modification of PHBHV appears to us as a real challenge for improving adhesion.

Our study has demonstrated an efficient green UV-photografting method for covalently modifying the surface of PHBHV film with hydrophilic monomers in aqueous media and in heterogeneous conditions with a cationic photoinitiating system. Micropatterning of PHBHV film provides the opportunity to develop microdevices for allowing cells to grow at specific locations. Such a procedure can be used for other monomer-containing chemical functions, improving their ability for cellular interaction.



D.L. Versace, P. Dubot, P. Cenedese,J. Lalevee, O. Soppera, J.P. Malval, E. Renard and V. Langlois, Green Chemistry, 2012, 14, 788-798

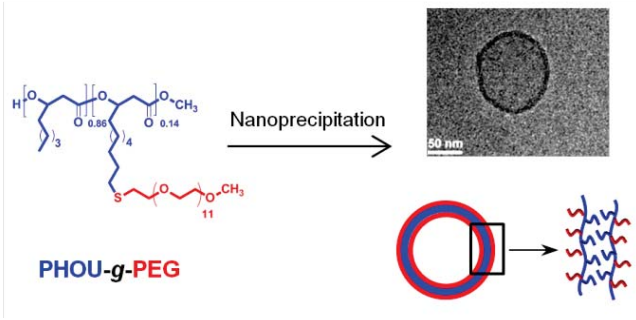
Contact: versace@icmpe.cnrs.fr

Bio-Materials

Poly(3-hydroxyalkanoate)-derived Amphiphilic Graft Copolymer for the Design of Polymersomes

Polymeric vesicles, the so-called polymersomes, have attracted considerable interest in the past decade regarding their potential applications in drug delivery, gene therapy or as model biomembranes. Mimicking natural liposomes, they are formed by the self-assembly of amphiphilic copolymers, providing more stable structures with improved mechanical properties.

Poly(3-hydroxyalkanoates) (PHAs) constitute a class of natural biocompatible and biodegradable polyesters. This article presents a straightforward synthesis of amphiphilic graft PHAs using click chemistry (thiol-ene addition) from unsaturated hydrophobic PHAs, noted PHOU, and hydrophilic poly(ethyleneglycol) (PEG). The copolymers have been demonstrated to form well-defined polymersomes in water by cryo-transmission electron microscopy. Moreover, they exhibited narrow particle size (average diameter 65 nm) and high stability upon dilution, making them promising structures for drug delivery applications. New biodegradable and biocompatible polymersomes are thus of particular interest for biomedical applications.



J. Babinot, J.-M. Guigner, E. Renard and V. Langlois
Chemical Communications, 2012, 48, 5364-5366

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HighLights

ICMPE acknowledges the contribution of several of its members in the writing of reviews, books and book chapters:

In the series "Materials and Metallurgy" directed by A. Pineau and edited by Lavoisier/Hermes*, is published under the supervision of Louisette Priester "**Joints de grains et plasticité cristalline**", with contributions from J.-P. Couzinié, S. Lartigue-Korinek and L. Priester, researchers at the MCMC group. This book is also available in English: "**Grain Boundaries and Crystalline Plasticity**", edited by Louisette Priester and published by Wiley/ISTE.
*Collection "Mécanique et Ingénierie des Matériaux" (MIM).

Louisette PRIESTER, Professor Emeritus of the University of Paris XI and researcher from the MCMC group, is also the author of a recent book "**Grain Boundaries - From Theory to Engineering**" published by Springer Publishing in their *Series in Materials Science*.

J. Zhang, F. Cuevas and M. Latroche from the CMTR group are co-authors with the group of J. Huot in Canada and T. Jensen in Denmark of a review article on "**Mechanochemical Synthesis of Hydrogen Staorage Materials**". This review will be published in Progress in Materials Science 2012
http://dx.doi.org/10.1016/j.pmatsci.2012.07.001

C. Godart from the CMTR Group, S. Bühler-Paschen and Yu.N. Grin are the authors of the chapter 9 " **Recent trends in the development of thermoelectric materials with complex crystal structures**" in "Complex Metallic Alloys - Fundamental and Applications", Edited by J.-M. Dubois and E. Belin-Ferré - Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, p. 365, 2011.

ICMPE congratulates its researchers for their awards:

Yannick Champion (Dir. of Res. at the MCMC team and lecturer at the University of Evry) and Jean-Michel Frund (EDF-CEIDRE) have been awarded the "Lavoisier for Apprenticeship" Prize by Gérard Ferey, gold medal of CNRS, for their excellent supervision of apprentice Franck Mukuna.
As president of its scientific comitee, Yannick has also organized "Les Journées Annuelles de la SF2M", 29 - 31 October 2012 at Chimie ParisTech 11 (Paris) and coordinated a national Action Training of CNRS on Fundamental Metallurgy in Aussois, 22-25 October 2012.

The article "Metal-assisted chemical etching of silicon in HF-H_2O_2, by **C. Chartier, S. Bastide, C. Lévy-Clément**" has been recognised in the "Top-25 most cited articles" as published in Electrochimica Acta during 2008-2009. The Top Cited Award has been delivered at the 62nd Annual Meeting of the International Society of Electrochemistry in Niigata, Japan.

Conference organized by ICMPE

ICMPE organizes its workshop « Materials for Energy » on Friday 7 December 2012 with focus on **"Materials for the Automotive Industry"**. Invited speakers: Cédric De Vaulx (Valéo), Pierre Tran Van (Renault), Patrice Simon (CIRIMAT), Christophe Goupil (CRISMAT), Olivier Delcourt (PSA).
Location: ICMPE's auditorium, 9h30-17h, Thiais. Coordinators: J.-P. Pereira-Ramos, F. Cuevas, L. Mazerolles.

ICMPE News

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