



A European COST Action on "Nanostructured materials for solid-state hydrogen storage" has been launched last 25/10/2011. This Action aims to foster European research cooperation and exchange of scientific knowledge in the field of hydrogen storage in nanoscale materials. At this stage, 19 European countries participate in this Action which is coordinated by Dr. Amelia Montone (INEA, Italia). The French members in the Action Management Committee are Prof. Fabrizio Cleri from University of Lille I and Dr. Fermin Cuevas from ICMPE/CNRS. More information is available at http://www.cost.esf.org/domains_actions/mpns/Actions/MP1103

ICMPE and NEXTER (industrial company) organised on September 7-9, sponsored by UPEC and the SF2M (Société Française de Métallurgie et de Matériaux), the 20th Technical meeting of the European Society DYMAT (European association for the promotion of research into the dynamic behaviour of materials and its applications) on the specific topic of **MECHANICAL BEHAVIOUR OF NANOMATERIALS, METALLIC GLASSES AND ARCHITECTURALLY DESIGNED MATERIALS.**



This international symposium was held at the Maison de la Chimie in Paris with about 50 attendants from industries, academic research laboratories, academies of sciences of different countries, the French academies of science and technologies. Outstanding presentations and discussions have emphasized the promising perspective for potential applications of these new types of metallic materials. The symposium was successful and the organisers wish to thank all attendants, speakers and sponsors, for their support and participation.

ICMPE News

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International Newsletter

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Editorial

The end of 2011 brought significant changes to ICMPE. First of all, Prof. Patrick HEMERY, former Director of our Institute has decided to retire and to move to other activities. We really appreciated his involvement in science and management and his human qualities over the last three years in our campus and we want to express him our warm thanks for the work he has accomplished. On December 14, a ceremony was held at the Department of Chemistry at the IUT de Vitry-sur-Seine and this was an opportunity for all his friends and colleagues to celebrate his long career and wish him all the best for the future. ICMPE is now halfway through its mandate and the time has come for a new period with a new management team of the Institute fixing the course of the next three years. I want to thank Valérie Langlois, Professor at UPEC, who has accepted to take over the position of deputy director and to share with me the difficult task, but exciting, to lead the Institute. This team will be completed in spring by a new General Secretary in charge of the administrative affairs. With this renewed management team, we can look forward with confidence with the aim to bring ICMPE at the highest level.

Several actions have already been launched to prepare the future. ICMPE is a partner in two proposals for laboratories of excellence "labex" in the frame of the governmental "Initiative d'Excellence".

Michel Latroche,
Director of ICMPE

The first one, called METACHEM (Chemistry for Metallic Materials of the Future) has the ambition to create an internationally renowned centre in the field of Chemistry for Metallic Materials.

The second one, (MMCD for Multi-Scale Modelling and Experimentation of Materials for Sustainable Construction) aims at structuring a group which will bring together leading researchers in engineering, physics, applied mathematics, statistics, rheology of pastes or granular media, mathematical modelling for complex physical systems and molecular simulations on the topic of civil engineering and environmental materials.

Beside these two projects, other actions have been conducted by scientists of ICMPE regarding European programs, COST and ITN actions, ANR applications and so on. At the beginning of this year, we make the wish that most of these actions will be successful and that our research activities will be brought at their better level for the coming years.

Finally, we want to congratulate Dr. Mohamed Guerrouache who has just been awarded the thesis prize from the University of Val de Marne for his PhD work dealing with "the synthesis of new versatile monolithic phases based on N-acryloxysuccinimide for applications in electrochromatography".



UNIVERSITÉ PARIS-EST CRETEIL VAL DE MARNE

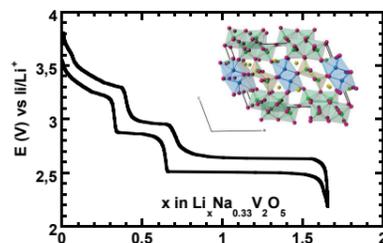
The peculiar structural behaviour of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ upon electrochemical lithium insertion

The structural response of the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ active material in a composite electrode is determined during discharge in the 3.8/2.2V potential range ($x < 1.66$ in $\text{Li}_x\text{Na}_{0.33}\text{V}_2\text{O}_5$) using X-ray diffraction combined with Raman microspectrometry. In spite of the existence of three well defined voltage plateaus, we provide evidence here for very weak structural changes throughout the lithium intercalation process. They consist in a single phase behaviour characterized by small variations in unit cell parameters a, b, c, V, β ($< 2\%$). At the atomic scale, only slight distortions are recorded by Raman microspectrometry.

These overall negligible structural changes strongly contrast with the successive emergence of narrow one-phase and wide biphasic regions usually described for attractive cathodic materials for lithium and lithium-ion batteries (e.g. $\text{LiCoO}_2, \text{LiMn}_2\text{O}_4, \text{LiFePO}_4, \text{V}_2\text{O}_5$). In the latter case, the order of magnitude in unit cell parameters is often more important. In that sense, the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ bronze constitutes an unusual example of host lattice the properties of which can be explained by its rigid 3D tunnel structure.

This peculiar behavior highlights the interest of such 3D host lattice to minimize the structural stress induced by lithium insertion. The present findings demonstrate the reliability of a lithium filling scheme in the $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ 3D host lattice involving no phase transition in a remarkably wide Li composition range. Indeed, three Li ordering processes corresponding to the successive filling of vacant sites by minimizing coulombic interactions are shown to govern the working potential of $\text{Li}_x\text{Na}_{0.33}\text{V}_2\text{O}_5$.

The kinetic behaviour, showing a decrease of chemical Li diffusion from one ordering process to the other one, can also be explained. The slowest diffusion is observed during the third process, i.e. when the repulsive coulombic interactions are the highest, and as a consequence the cycling behavior is mainly affected in this region. This result raises the question about the key factor responsible for the shape of the working potential and how to account, from an electrochemical point of view, for the presence of one phase and two phase-region.



First discharge-charge cycle of a $\text{Li}_x\text{Na}_{0.33}\text{V}_2\text{O}_5$ electrode in the 4/2.15 V potential range (C/20 rate), in inset: 3D crystal structure of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$

R. Baddour-Hadjean, S. Bach, N. Emery and J. P. Pereira-Ramos, *The peculiar structural behaviour of $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ upon electrochemical lithium insertion*, *J. Mater. Chem.* 2011, 21, 11296-11305

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Nanostructured Si/Sn-Ni/C composite as negative electrode for Li-ion batteries

Research on intermetallic compounds (IMCs) as anode materials for lithium-ion batteries presents great interest. These IMCs exhibit better electrochemical stability compared to pure elements, which suffer from mechanical failure when forming lithium alloys. Suitable intermetallic compounds consist of an element that reacts with lithium for capacity and another one, inactive toward Li but conductive and able to accommodate volume changes. Unfortunately, this concept has as a drawback: the concomitant diminution of the electrode capacity. However, combination of two active elements is also possible and interesting thanks to the alloy formation potential difference between the two elements. In this case one buffers the volume expansion of the other and vice versa. In this study, we propose the development of two-phase nanostructured composite formed by highly capacitive elements and IMCs.

The selected nanocomposite has as nominal composition $\text{Ni}_{0.14}\text{Sn}_{0.17}\text{Si}_{0.32}\text{Al}_{0.037}\text{C}_{0.346}$. It consists of Si particles with a typical size of 150 nm embedded in poorly crystallized, nanostructured and complex multielemental matrix. This matrix contains 6 nm in size Ni_3Sn_4 precipitates and disordered carbon as major phases with minor amounts of $\beta\text{-Sn}$ and amorphous Si-Ni phases. The composite is synthesized by ball-milling of Si, carbon and Ni_3Sn_4 powders where Ni_3Sn_4 has been previously prepared by powder metallurgy. A TEM image is given (figure 1) showing the nanocomposite microstructure obtained after 20 h milling. In this study, Chemical and structural properties of the nanocomposite have been determined by X-ray diffraction (XRD), ^{119}Sn Transmission Mössbauer Spectroscopy (TMS),

scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Electrochemical evaluation shows that this composite is a very promising anode material for Li-ion batteries since it has a high reversible capacity reaching 920 mAhg^{-1} , with reasonable reversible capacity retention (0.1% loss/cycle) over 280cycles (figure 2).

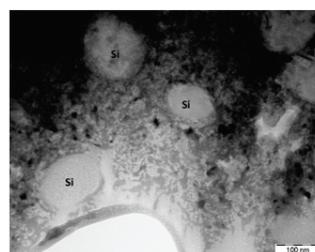


Figure 1: TEM image of the nanostructured $\text{Ni}_{0.14}\text{Sn}_{0.17}\text{Si}_{0.32}\text{Al}_{0.037}\text{C}_{0.346}$ composite showing the microstructure.

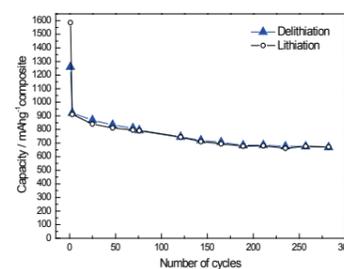


Figure 2: Charge and discharge capacities vs. cycle number of the 20 h - milled $\text{Ni}_{0.14}\text{Sn}_{0.17}\text{Si}_{0.32}\text{Al}_{0.037}\text{C}_{0.346}$ composite at C/50.

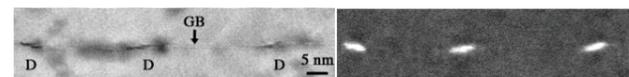
Z. Edfouf, F. Cuevas, M. Latroche, C. Georges, C. Jordy, T. Hézègue, G. Caillon, J. C. Jumas and M. T. Sougrati, *Journal of Power Sources*, 196 (2011) 4762-476.

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HAADF study of the relationship between intergranular defects structure and yttrium segregation in an alumina grain boundary

Both the structure and chemistry of grain boundaries (GB) determine numerous materials properties. On one hand, GB segregation depends on the intergranular structure, on the other hand, GB segregation itself can modify the GB structure and GB distribution in a polycrystal, and, ultimately, the polycrystal properties. In alpha alumina, it is well known that additions of rare earth elements strongly modify the plastic properties. Yttrium doping has a beneficial role in the creep of alumina; it yields a significant decrease in creep rate, attributed to a decrease in GB diffusion. However the creep rate with Y-doping is much further reduced than could be expected from this effect.

The general aim of our experiments is to localise the segregated element in a grain boundary at the atomic scale. Z-Contrast (HAADF) imaging in a STEM reveals huge and ordered yttrium segregation at the core of intergranular dislocations, namely disconnections, in a rhombohedral twin in alumina. The defects accommodate the tilt deviation from twin orientation and present a large step height. In the undoped bicrystal the dislocations appear most often dissociated into partials that delimit grain boundary segments with alternating structure. In the doped bicrystal, a strong yttrium segregation appears along the step, extending over several planes normal to the twin plane.

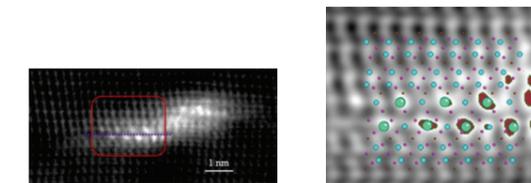


Cs-corrected STEM Bright Field and HAADF images of an Y-doped alumina bicrystal. Both images exhibit the rhombohedral twin composed of a perfect twin part and a pseudo-periodical disconnection (D) network. The HAADF image clearly illustrates the segregation of Y to all the disconnections

Yttrium is segregated to the faulted part of the defect and to the partial disconnection cores. The dark field image below resolves

particularly well the yttrium rich columns in the left part of the defect, and yttrium distribution clearly adopts a 2-dimensional structure as follows:

Along the GB, very bright spots alternate with less bright spots, and the brightest spots are translated between the upper and lower crystal. A model for this yttrium-rich structure corresponds to the YAIO_3 compound in the $[10\bar{1}]$ projection. The stress field created by the dislocations is the driving force for the migration of atoms towards them, and they are then "pinned" by the segregated species.



Dark field images of one disconnection : To the left of the defect, the yttrium distribution appears structured. In the enlarged part where the brightest spots are coloured in red, green dots correspond to yttrium-rich columns

Two important conclusions arise from these results: First, the initial steps of precipitate nucleation at a GB dislocation core are emphasized. Then, the formation of such an ordered compound must reduce species diffusion, strongly supporting the hypothesis that a reduced creep rate results from a decrease in dislocation mobility.

Sylvie Lartigue-Korinek, Danièle Bouchet, Andrew Bleloch and Christian Colliex, *Acta Materialia*, 59 (2011) 3519-3527

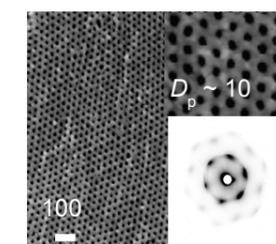
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Functionalized ordered nanoporous polymeric materials: From the synthesis of diblock copolymers to their nanostructuration and their selective degradation

Over the last decade, designing organic porous materials with controlled pore sizes and narrow pore size distributions as well as desired functionalities has attracted increasing attention due to the established and potential applications of these materials in many areas, including advanced filtration or separation techniques, heterogeneous supported catalysis, as well as template-assisted synthesis of nanomaterials. Organic porous materials present unique properties compared to their inorganic nanostructured analogues, such as tunable mechanical properties, ease of functionalization, and mostly lower production cost. Despite many investigations in this field, it is still a major challenge to engineer mesoporous polymer frameworks with tunable porosity and functionality while maintaining good mechanical properties and high chemical stability of the organic matrices.

Self-organized block copolymers have received great attention and they have been seriously considered for nanotechnological applications. Such macromolecular architectures can be effectively utilized as nanostructured precursors to functionalized ordered mesoporous polymeric materials. Novel nanoporous polystyrene frameworks with carboxylic acid (COOH)-coated pore walls were obtained from the selective degradation of the polyester block in polystyrene-block-poly(D,L-lactide) (PS-*b*-PLA) diblock copolymers. By resorting to an asymmetric difunctional initiator, an orthogonal atom transfer radical polymerization (ATRP) / ring-opening polymerization (ROP) tandem approach enabled the synthesis of such diblock copolymers with a carboxyl group at the junction point between both blocks. Upon the shear flow induced by a channel die processing, highly oriented copolymers were afforded as evidenced by small-angle X-ray scattering (SAXS).

Under mild alkaline conditions, the quantitative hydrolysis of the PLA nanodomains yielded ordered mesoporous materials containing nanoscopic channels lined with chemically accessible and modifiable COOH functional groups. The PS-*b*-PLA precursors were carefully analyzed by size exclusion chromatography (SEC) and ^1H NMR, while the resulting porous frameworks were investigated by scanning electron microscopy (SEM) and nitrogen sorption porosimetry. The potential applications of such functional nanoporous materials are mainly expected in the areas of heterogeneous supported catalysis, nanomaterials synthesis, and chemistry in confined media.



SEM micrograph of nanoporous material derived from PS-*b*-PLA copolymer oriented by channel die processing, and corresponding 2-D SAXS pattern.

D. Grande, J. Penelle, P. Davidson, I. Beurroies, and R. Denoyel, *Microporous and Mesoporous Materials*, 140 (2011) 34-39.

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