Editorial

In this issue of the ICMPE Newsletter, we collected five highlights describing our recent scientific activities. Covering various fields, from magnetism to electro-chemistry, surface modification of polymers to multi-component organic chemistry, we want to give you here an overview of our multidisciplinary approach to chemistry and materials science.

Today, a good basic research cannot be achieved without strong and recognized international scientific relations. We are proud to be partners of the Franco-Russian International Associated Laboratory (LIA) MEIPA, which got a very good score at the last assessment. We are also involved in three Marie Curie Actions (ITN), showing our ability to prepare young scientists from around the world to become the next generation of researchers.

Finally, there is no good science without proper dissemination of results. We put a lot of effort in organizing international (E-MRS) and national (Li-battery) workshops bringing together researchers from different backgrounds around common scientific challenges that we want to tackle together.

Michel Latroche,
Director of ICMPE

ICMPE, a partner of choice in the Franco-Russian International Laboratory “Ion-Exchange Membranes and related processes”

The research group on “Porous Materials and Membranes” from the Polymer Complex Systems Team at ICMPE has been working for over 10 years in collaboration with different Russian and French partners, in particular with the European Membrane Institute at Montpellier (IEM), the Membrane Institute at Kuban State University in Krasnodar (MI-KubSU) and the Institute of General and Inorganic Chemistry of Russian Academy of Sciences in Moscow (IGIC-RAS). The collaboration between these four laboratories has led to the development of a Franco-Russian International Associated Laboratory (LIA) for the period 2011-2014. The LIA focuses on Ion Exchange Membrane and Related Processes and has been ranked first in the final evaluation of the 27 structures of its kind in France.
**Energy Storage**

**Electrochemical properties of bias sputtered LiCoO$_2$ thin films in liquid electrolyte**

Combining a high working pressure, a bias effect and a moderate post-annealing treatment at 500°C, high performance LiCoO$_2$ thin films have been prepared using RF sputtering in a wide range of thickness 0.25 to 3.6 μm. A 450 nm thick film can work without any polarization at 2C rate, delivering then a specific capacity of $\approx 50$ μAh cm$^{-2}$ μm$^{-1}$ with a capacity retention of 90% after 50 cycles. This finding is remarkable when compared to the capacity retention of 50-70% usually achieved with sputtered films regardless of the post-annealing temperature. The present biased LiCoO$_2$ films constitute high rate cathode materials since 83% of the maximum capacity is recovered at 4 C and still 73% at 8 C. The films can sustain up to 40 C without damaging its further cycling behavior. Such attractive electrochemical characteristics have never been reported as yet.

The experimental procedure to produce such sputtered films has been proven to be highly reliable and reproducible, as shown by the linear increase of capacity with thickness over the range 0.25-3.6 μm. This allows capacities as high as 200 μAh cm$^{-2}$ to be reached with a 3.6 μm thick film. This capacity value is the highest known as yet in liquid electrolytes.

**Bio-Materials**

**Versatile Photochemical Surface Modification of Biopolyester Microfibrous Scaffolds with Photogenerated Silver Nanoparticles for Antibacterial Activity**

Silver-containing PHBHV-g-PMAA microfibrous scaffolds with antibacterial activity were successfully engineered, according to an environmentally sustainable “green chemistry” approach. Our study has demonstrated a new efficient method for covalently modifying the surface of PHBHV electrospun fibers, under light activation and in aqueous media.

The carboxylic groups of the resulting PMAA chains were used as efficient capping agents to promote homogeneous size-control and dispersion of silver nanoparticles on the PHBHV surface. Ag NPs were in-situ generated upon light irradiation, according to a fast photoreduction process.

PHBHV microfibrous scaffolds including silver nanoparticles led to a tremendous inhibition of the adhesion of Escherichia Coli and a reduction by 98 % of the adherence of Staphylococcus aureus. This new route of grafting could be further used to broaden the application portfolio of PHAs.

![Scheme of the functionalized PHBHV-g-PMAA fibers by silver nanoparticles.](image)


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**Advanced Materials**

**Study of the magnetic and electronic properties of nanocrystalline PrCo$_3$ by neutron powder diffraction and density functional theory**

The progress in permanent magnets has been tremendous during the last few decades, particularly after the advent of rare earth permanent magnets. Most of the time, the transition metals provide high Curie temperature and saturation magnetization, and the rare earth elements, high magnetocrystalline anisotropy. Among nanocrystalline magnets based on rare earth $R$ and transition metal elements $M$, the $RM_3$ compounds (PuNi$_3$) have been the subject of many studies during the last decades.

In this study, we report the elaboration of nanocrystalline PrCo$_3$ by high-energy milling. The structural and magnetic properties were studied by X-ray and neutron powder diffraction at different temperatures as well as by magnetic measurements. In addition to the experiments, a theoretical investigation by Density Functional Theory (DFT) has been made. We present for the first time a comparative study of experimental and calculated data for PrCo$_x$ compounds ($x=2,3,5$). The two approaches both indicate a strong magnetic anisotropy in PrCo$_3$, however, the observed discrepancies on the magnetic moments show the limits and difficulties to correlate both experimental and theoretical representations of the magnetic properties.

![Temperature dependence of lattice parameters by in-situ neutron diffraction](left), Density of state with spin polarization of PrCo$_3$ (right).


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**Materials for Life science**

**Site-specific immobilisation of gold nanoparticles on a porous monolith surface by using a thiol-yne Click photopatterning approach**

Combining metallic nanostructures with monolithic polymers provides fascinating opportunities for the design of smart heterostructures for life sciences applications. Indeed, separation, concentration and detection of biomolecules can be performed in a simple and efficient way.

We have developed a new photochemical method for the surface functionalisation of porous monoliths allowing the site-specific immobilisation of gold nanoparticles at the pore interface. To establish the method, chelating primary amino groups were photochemically attached to alkyne-functionalized monolith surface through thiol-yne radical addition reaction providing hydrophilic and chelating interface.

Moreover, the method allows a good control of the dispersion of the gold nanoparticles at the monolith’s surface allowing the tuning of the interface properties.

We anticipate that this method offers great promise for the controlled design of microdevices based on nanostructured polymer hybrids and is easily adaptable to microfluidic chip technology.

![Spatial control of the chemical modification and further nanostructuration of monolith surface through unprecedented thiol-yne click photopatterning.](right)


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**In the frame of a State-Region Contract Plan, ICMPE strengthens its scientific equipment facilities with**

- an **X Ray Photoelectron Spectrometer** (P. Dubot, MCMC) for the surface characterization of metallic alloys, oxides nanoparticles and functionalized polymers thin films used in various fields like biomaterials or corrosion of metals (K$_\alpha$ ThermoElectron, spot size 30-400 μm, monochromated Al K$_\alpha$ source) ;

- a **Mössbauer Absorption Spectrometer** (L. Bessais, CMTR). Based on the phenomenon of the recoil-free, resonant absorption and emission of gamma rays (resonance quantum effect), this non-destructive technique allows studying the valence states of atoms, their chemical bonds and their coordinated in solid phases ;

- a **Sputtering Machine** (L. Bessais, CMTR) for coating and deposition of magnetic thin films or multilayers. It is equipped with three magnetrons for 2” targets, each operated with a DC or RF plasma 300 W power supply. This sputtering system can deposit 3 items sequentially or simultaneously (co-sputtering).
**Sustainable Chemistry**

**A Four-Component Synthesis of β-Amino Esters**

Multicomponent reactions are powerful processes of organic synthesis as they allow a straightforward access to complex products starting from readily available materials, thus paving the way of modern chemistry. Unfortunately, their development is generally hampered by their intrinsic complexity given the important number of possible concurrent pathways at each elemental reaction step. As a consequence, only a very limited number of multicomponent reactions involving four or more reagents have proved to be reliable enough to enter among the usual synthetic tools available to organic chemists.

In this article, we describe the first example of a four-component reaction involving organometallic species generated in situ from aryl (or vinyl) halides. This Mannich-related reaction allows the preparation of β-amino esters from aldehydes, amines, acrylates and halides through a conjugate addition/aza-aldol domino reaction sequence.

The scope of this Mannich-like reaction is demonstrated through the formation of diversely-substituted β-amino esters. A possible reaction mechanism emphasizing the crucial role of zinc salts is also discussed.

![Chemical structure](image)

The four-component reaction and selected examples of the obtained products.


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**Conferences and Workshops**

ICMPE has organized the annual workshop “Lithium Batteries - Ile-de-France” on Tuesday 10th of September, 2013. Participants: Academics (UPEC, UPMC, CNRS, CNAM, ENSCP, Ecole Polytechnique, SOLEIL) and Industries (Peugeot). Contact: J.-P. Pereira-Ramos and R. Baddour-Hadjean (GESMAT).

Up-Coming soon

In the framework of the European COST-Action MP1103 on hydrogen storage, a workshop “Hydrogen storage: research activities and industrial requirements” will be held at ICMPE on April 9th-10th, 2014. Contact: F. Cuevas (CMTR).

The national workshop “Thermodynamics of Materials at High Temperature”, related to the activities of the GdR of the same name will take place at ICMPE on January 16th-17th, 2014. Contact: J.-M. Joubert (CMTR).

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**ICMPE News**

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**Latest reviews, books or book chapters by ICMPE researchers:**


http://dx.doi.org/10.1016/j.colsurfa.2012.11.043


http://dx.doi.org/doi:10.1016/j.colsurfa.2013.04.013

**Invited Scientists**

The GESMAT team thanks Pr. Mikhail Smirnov from the Fock Institute of Physics (Saint-Petersburg State University) for his scientific input on the theoretical developments for understanding the Raman spectra of Li intercalation compounds during his stay at ICMPE as guest professor in 2013.

**Adhesion to the French National Chemical Library**

The ICMPE is proud to announce his recent adhesion to the French National Chemical Library "Chimiothèque Nationale", (CN) through the signature of a convention between the GIS CN and the University Paris-Est Créteil. Created in 2003, the CN federates collections of synthetic products, natural compounds and extracts from French academic laboratories and promote their scientific/industrial valorization.