ICMPE
Institut de Chimie et des Matériaux Paris-Est
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UPEC Connaissance - Action
UNIVERSITÉ PARIS-EST CRÉTEIL VAL DE MARNE
Newsletter
15
December 2023

Editorial

After four years of ICMPE direction, we are leaving our management duties with the satisfaction of noting the positive transformations carried out by the laboratory. The new dynamics notably results from the structuration of the Unit into two scientific departments, "Metallurgy and Inorganic Materials" (M2I, 6 thematic groups) and "Molecular Chemistry and Macromolecular Materials" (C3M, 4 thematic groups), focusing on discriminating research themes that allow for the emergence of novel projects.

In parallel with the two research support departments, *i.e.* administrative and technical ones, a new "partnership and valorization" department has been created since May 2023 following the recruitment of a transfer engineer on a fixed-term contract for 3 years. This important recruitment for the promotion of technological platforms to industrials was made possible thanks to the support of the DGDI-CNRS in response to its "Platforms 2022" call for projects.

On the scientific front, our Unit is strongly supported by the PEPR "Decarbonized Hydrogen", co-led by the CNRS and the CEA, with in particular the coordination of the project targeted at solid hydrogen storage (SOLHYD) which brings together a consortium of 6 CNRS Units and 2 CEA laboratories. This national strategic program is heavily endowed; for our Unit alone, seven doctoral contracts have been launched for the period 2022-2026. The development of new materials for hydrogen storage has also been strengthened by the support of UPEC with a Junior Professor Chair (CPJ) since September 1st, 2022. In addition, our laboratory has begun to benefit from the CPER for the period 2022-2027 with the Step Forward Micro project with a €1.6M funding by the Ile-de-France Region to develop the "Microscopies" platform. A first operation was carried out with the acquisition of a new electron energy loss spectrometer (EELS), a filtered imaging system installed on the transmission electron microscope. Our Unit was also the recipient of the SESAME call for projects of the Ile-de-France Region for the purchase of a new Spark Plasma Sintering (SPS) equipment in a glove box environment which will take place in the forthcoming months, thanks to the co-funding of UPEC, CNRS, and the nine laboratories using the Ile-de-France SPS platform located at ICMPE. In addition, the Unit's dynamics on responding to ANR calls for projects continued on the momentum of previous years, with 6 projects funded (1 JCJC, 4 PRC, 1 PRCE) in 2023. This good dynamics of the Unit is also visible at the local, regional and national levels with projects supported in response to various competitive calls for projects: post-doctoral fellowship from UPEC, LabEx MMCD (materials for sustainable construction) associated with the I-SITE FUTURE project of ComUE Paris-Est Sup, DIM MaTerRe (eco-responsible materials) of the Ile-de-France and Emergence@INC2023 from CNRS. Finally, ICMPE has fostered the creation and the launch of a Graduate Program on "Materials for the future and Management of Enterprise Risks" (GP MMER) supported by UPEC, namely an international and interdisciplinary program of excellence at the Master's and PhD levels.

Last but not least, we would like to thank all permanent and non-permanent staff for their daily involvement and support throughout these years. We wish many successes and all the best to the future director, Jean-Marc Joubert (CNRS Research Director), who will take up his new position starting from January 1st, 2024.

Daniel Grande ICMPE Director • **Ivan Guillot** Deputy Director

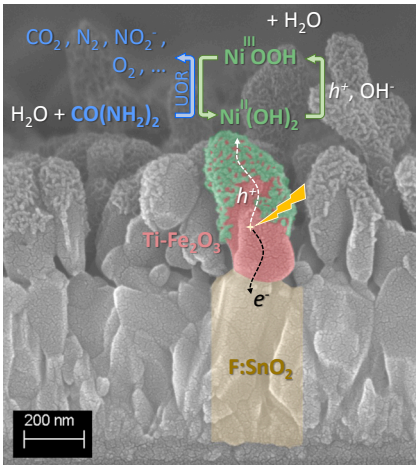
Energy and Environment

Photoelectrocatalytic conversion of urea under solar illumination using Ni decorated Ti-Fe_2O_3 electrodes

To reduce the energy cost and environmental impact of biological nitrogen removal in wastewater treatment plants, it would be advantageous to treat urea contained in urine at the source.

In this perspective, FTO/Ti-Fe_2O_3 photoelectrodes with Ni as catalyst were developed and tested for urea photoelectrocatalytic oxidation under solar illumination. The SEM images in the figure below shows how the Fe_2O_3 nanorods could be covered with a NiOOH layer by a photoelectrodeposition method. Gains up to 0.50 V in oxidation onset potential vs. metallic Ni are obtained, which allows H_2 production (cathode) at a lower cell potential.

In situ optical transmission measurements (based on NiOOH light absorption) during electrochemical cycling allowed to evaluate the state of active Ni sites and confirmed that urea oxidation mechanism is of EC type. Photoelectrolyses give faradaic efficiencies of 10-18% and 9-35% for N_2 and O_2 formation, respectively. A significant and unexpected NO_2^- production (~65%) is detected indicating another or incomplete reaction pathway. The photoelectrocatalytic removal of nitrogen from urea solutions is demonstrated but requires catalysts with higher selectivity towards N_2.



L. Rebiai, D. Muller-Bouvet, R. Benyahia, E. Torralba, M. Lopez Viveros, V. Rocher, S. Azimi, C. Cachet-Vivier, S. Bastide, Electrochimica Acta, 2023, 438, 141516

Contact : stephane.bastide@cnrs.fr

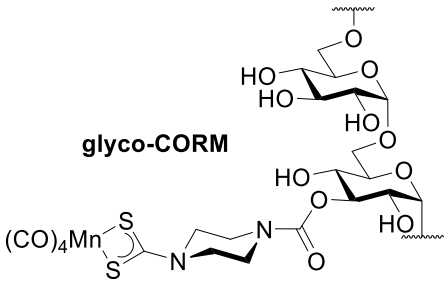
Therapeutic Chemistry

Development of carbon monoxide-releasing molecules conjugated to polysaccharides (glyco-CORMs) for delivering CO during obesity

Metal carbonyls have been developed as carbon monoxide-releasing molecules (CO-RMs) to deliver CO for therapeutic purposes. A manganese-based CO-RM was reported to exert beneficial effects in obese animals by reducing body weight gain, improving glucose metabolism, and reprogramming adipose tissue towards a healthy phenotype.

The article reports on first examples of glyco-CORMs, obtained by grafting manganese-based CO-RMs on dextrans (70 and 40 kDa), polysaccharides deriving from glucose, also known to target adipose tissue. Glyco-CORMs proved to efficiently deliver CO to cells in vitro with higher CO accumulation in adipocytes compared to other cell types.

In vivo studies showed that oral administration of two selected glyco-CORMs resulted in CO accumulation in various organs, including adipose tissue. In addition, a glyco-CORM administered for eight weeks elicited anti-obesity and positive metabolic effects in mice fed a high fat diet.

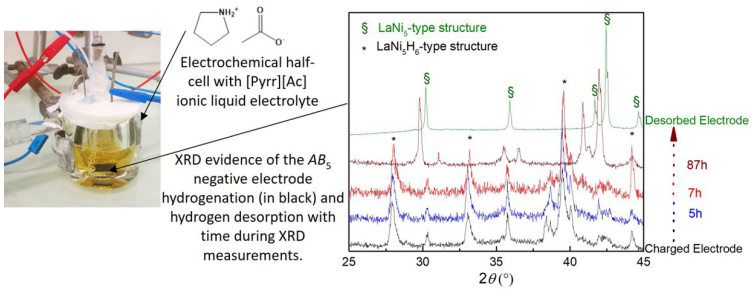


S. Mohan, L.-A. Barel, D. E. Benrahla, B. Do, Q. Mao, H. Kitagishi, M. Rivard, R. Motterlini, R. Foresti, Pharm. Res., 2023, 191, 106770.

Contact : michael.rivard@cnrs.fr

Proton Exchange Batteries

Toward new proton exchange batteries based on ionic liquid electrolyte: metal hydride electrode / electrolyte coupling



The voltage of an alkaline electrolyte-based battery is limited by the electrochemical stability window of water. As an alternative to water, protic ionic liquid (IL)-based electrolytes have shown excellent conducting properties as well as a wide electrochemical stability window, and can therefore be implemented in protonic batteries.

In this work, included in the frame of the ANR project H-BAT (ANR-21-CE50-0030, New concept of protonic battery) we present the physicochemical properties of different ILs that have been selected for their potential use in protonic batteries; namely, one aprotic IL (1-ethyl-3-methylimidazolium acetate [EMIM][Ac]) mixed with acetic acid as proton donor, two protic ILs, the pyrrolidinium formate [Pyrr][F] and the pyrrolidinium acetate [Pyrr][Ac] and mixtures with their parent acid or base.

The electrochemical properties of an AB5-type compound as negative electrode in a half-cell configuration using these ILs as electrolyte are then reported. A discharge capacity of 221 $mAh{\cdot}g^{-1}$ was attained at C/40 regime with low charge/discharge overpotential. Moreover, stable cycling performance was obtained by using [Pyrr][Ac] as IL, with an electroactivity window of 2.2 V enlarged compared to the one of KOH.

N. Chaabene, J. Zhang, M. Turmine, E. Kurchavova, V. Vivier, F. Cuevas, M. Mateos, M. Latroche, J. Monnier, J. Power Sources, 2023, 574, 233176.

Contact : judith.monnier@cnrs.fr

Past events

• HyCARE Project Final Event: an innovative approach for renewable energy storage, now reality. Last April 21, 2023, this final event took place in Paris with an exhibition entitled "The HyCARE system. Opportunities and challenges of the energy storage sector". Hosted by ENGIE Lab Crigen in cooperation with CNRS, it aimed to show the main results of obtained during the HyCARE Project, supported by the Clean Hydrogen Partnership, and coordinated by the University of Turin. ICMPE was a major partner in this project, its mission being to develop alloys capable of reversibly absorbing hydrogen. Contact: F. Cuevas.

• The GdR HEA Summer School was held in Cargèse from September 11 to 15, 2023. Since 2019, the GdR has brought together chemists, mechanics, physicists and materials scientists from 15 laboratories (100 active members). ICMPE contact: Ivan Guillot.

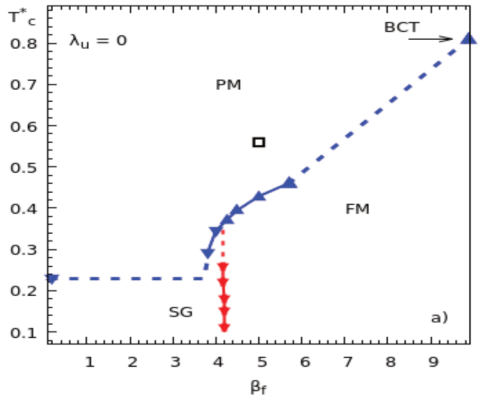
• ICMPE has hosted the 12th workshop *Batteries Lithium en Île-de-France*, organized by R. Baddour-Hadjean, J.P. Pereira-Ramos and G. Bernari, (M2I department) on December 13, 2023 at ICMPE.

Magnetic nanoparticles

Ferromagnetic frozen structures from the dipolar hard spheres fluid at moderate and small volume fractions

The importance of the modeling of magnetic nanoparticles (MNP) properties stems from the progress in experimental synthesis which leads to an increasing variety of superstructures with complex magnetic phases (ferromagnetic (FM) or spin-glass (SG) at low T.

Small enough MNP should be view as spherical particles bearing a constant magnetic moment interacting through the dipole-dipole interaction and the short-range hard sphere potential that mimics the steric effects. In the liquid state (ferro fluid) this corresponds to the dipolar hard sphere fluid (DHS). Both the DHS at sufficiently high-volume fraction and the perfect lattice of dipoles with FCC or BCT symmetry order at low temperature in a well-defined FM phase. This is also the case for disordered frozen distributions of particles at a volume fraction $\Phi > \Phi_s \approx 0.495$. At lower Φ, the FM order is destroyed, and a SG phase takes place. Here we show that the FM ordering can be restored at $\Phi > \Phi_s$ by considering frozen structures derived from the DHS in its FM state, i.e. at inverse freezing temperatures $\beta_f > \beta_c(\Phi)$ where $\beta_c(\Phi)$ is the inverse critical temperature of the ferro fluid. We show that even at $\Phi < \Phi_s$ the system orders in a well-defined FM phase for $\beta_f > \beta_c(\Phi)$. The figure below shows the phase diagram of the frozen dipolar hard sphere fluid in terms of the inverse freezing temperature β_f. The volume fraction is $\Phi = 0.45 < \Phi_s$. The induced anisotropy of the structure increases with β_f.

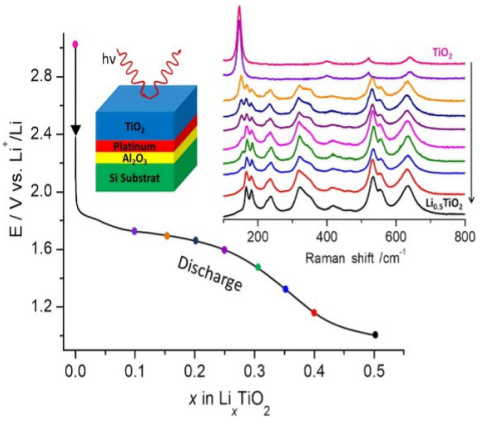


J.-G. Malherbe, V. Russier and J.-J. Alonso, J. Phys.: Condens. Matter, 2023, 35, 305802.

Contact : malherbe@u-pec.fr

Materials for Energy Storage

Electrochemical Lithium insertion into TiO_2 Anatase ALD thin films for Li-ion microbatteries: An atomic-scale picture provided by Raman spectroscopy



TiO_2 anatase is an attractive anode material for Li-ion batteries, due to its excellent structural stability, good cycling life, environmental friendliness, high safety, and low cost. This material has also received great interest as thin film negative electrode for Li-ion microbattery. However, while extensive research works have been reported on the Li intercalation mechanism in the composite powdered electrode, using mainly X-ray and neutron diffraction, the structural changes of TiO_2 thin film upon discharge-charge have not been explored yet.

In this work, Raman spectroscopy reveals the atomic-scale picture of electrochemical Li insertion into ALD deposited TiO_2 anatase thin films: The nucleation and growth of the $Li_{0.5}TiO_2$ phase is clearly observed. Relevant descriptors in the Raman spectra afford a reliable estimation of the lithium content in the thin film during the redox process.

The obtained results illustrate Raman spectroscopy is a powerful probe to scrutinize the Li insertion/extraction mechanism in TiO_2 thin films.

A. Bhatia, M. Hallot, C. Leviel, P. Roussel, J. P. Pereira-Ramos, C. Lethien, R. Baddour-Hadjean, Adv. Mater. Interfaces 2023, 10, 2202141

Contact : rita.baddour-hadjean@cnrs.fr

• The Fermi Federation organized two theme days in which ICMPE was involved: "Refractory alloys: for use at high temperatures" on June 23, 2023, at ICMPE, and "Historical Metallurgy" on December 13, 2023 at the Conservatoire des Arts et Métiers in Paris. ICMPE contact: Ivan Guillot.

• The GDR IAMAT organized a spring school in Roscoff, focusing on the use of machine learning in materials science, with 45 participants, mostly non-permanents. The school took place over 5 days, from April 17 to 21, 2023. ICMPE contact: Jean-Claude Crivello (member of the GDR assistant directors).

• The 3rd plenary sessions of the French Hydrogen Research Federation (FRH2) were held in La Réunion from May 22-26 2023. With 170 participants and 90 oral presentations by young doctoral students, internationally recognized researchers and industrialists, this year's event was a great success, thanks in particular to the members of the Federation board and the parallel session leaders, including F. Cuevas (ICMPE) and P. Derango (Institut Néel) for the "Storage" session.

• The *Réseau National de la Métallurgie* organized a new edition of "*La Métallurgie, Quel Avenir!*" from June 5 to 9, 2023 at the Grenoble INP on the Minatec site. It brought together the players in French metallurgy, both academic and industrial, to discuss common issues, from training to research, in thematic sessions and round tables, and to exchange views on major transformation challenges facing the sector. ICMPE contact: Mathilde Laurent-Brocq (Scientific Committee).

Distinctions

• Congratulations to **Ankush Bhatia** (M2I/BATTion) who is the **winner of the Paris-Est Sup thesis prize**, which recognizes every year the best thesis from each of its doctoral schools . Thesis topic: New insights into Li-ion batteries provided by Raman spectroscopy.
• We are also pleased to congratulate to **Jean-Philippe Couzinié** who has been awarded the 2024 Silver Medal by Acta Materialia. Recognized for the quality of his investigation in the field of High Entropy Alloys, Jean-Philippe will receive his award at the TMS 2024 conference in Orlando, Florida, where he will present his research at the Acta Materialia Symposium.

Welcoming our new faculty and staff members

• We welcome Dr **Aziz Ghoufi**, new professor of Physics at UPEC. Aziz obtained his PhD in physical chemistry from the University Blaise Pascal, Clermont-Ferrand, France, in 2006. Following two postdoctoral positions, he joined the Institute of Physics of Rennes in 2008. He is now set to work in the Modeling and Calculation group of M2I, focusing on the physics of interfaces and CO_2 capture from porous materials. His goal is to enhance the understanding of the microscopic mechanisms governing fluid structuring at the nanoscale.

• We are pleased to introduce **Laetitia Vois-Stevenin**, Transfer Engineer / Technical Sales Representative. Her role is to promote the Institute's technical platforms and to develop partnerships between ICMPE teams and industrial companies.

• We also welcome **Kadiatou Bah**, recruited as an Assistant Engineer position at UPEC. Kadiatou, who holds a Master's degree in Chemistry (Université Paris Diderot), will be working on the FST's chemistry technical platform and ICMPE's Measurement and Analyses of Materials (MAM) platform.

Graduate Program

In September 2023, UPEC launched a new Graduate Program in Chemistry, entitled **"Materials for the future and Management of Enterprise Risks"**, which aims to offer Master and PhD high level training, through international and interdisciplinary courses in materials science and in financial, economic and societal risk management. It benefits from the resources and infrastructures of ICMPE along with UPEC research units MSME and CERTES for materials science and IRG for management.

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

• A special issue entitled "Hydrogen-based Energy: Status and Prospects" of the Journal of Alloys and Compounds is dedicated to the memory of our colleague Dr. Michel Latroche, former director of ICMPE and a internationally recognized expert on hydrogen storage materials. Edited by V. A. Yartys and F. Cuevas, it contains 15 reviews and research papers presented as invited contributions at a memorial workshop held at ICMPE on June 13th, 5 of them by Michel's former ICMPE colleagues. **Journal of Alloys and Compounds, 2023, Vol. 937**.
• In the Techniques de l'Ingénieur collection, Mathilde Laurent-Brocq (ICMPE) and Lola Lilensten (IRCP), review the current life cycle of aluminum, and the solutions implemented for its recovery, sorting and recycling. The limits and weaknesses of the current material cycle are highlighted and discussed. ***Récupération et recyclage de l'aluminium - Stratégie*. TI, 2023, M2345 (HAL version)**.
• A. Fainleib, O. Grigoryeva, O. Starostenko, K. Gusakova, D. Grande, have published a book entitled **Thermostable Nanoporous Polycyanurates**, PH "Akademperiodyka," 2023 (ISBN 978-966-360-477-0), devoted to the synthesis, analysis of the structure and morphology, porosity parameters and physicochemical properties of heat-resistant nanoporous polycyanurates.
• G. Morales, H. Rodríguez-Tobías, V. Padilla-Gainza, K. Lozano, and D. Grande have published a book chapter entitled **"Harnessing the Potential of Fibrous Polyester Composites Meant for Bioactive Medical Devices"** in Green-Based Nanocomposite Materials and Applications; Avalos Belmontes F., González F.J., López-Manchado M.Á., Eds.; Springer Nature: Cham, Switzerland, 2023, pp.365-389.

Scientific communication

• On December 15, 2023 at UPEC, J.-M. Joubert, E. Torralba, F. Couturas, V. Paul-Boncour and G. Dieutegard from ICMPE took part in a Declics operation (Dialogues Entre Chercheur(e)s et Lycéen(ne)s pour les Initier à la Construction des Savoirs). This is a 1.5 h speed-meeting where groups of high-school students meet researchers and (post)doctoral students, engineers, technicians every 12 min to discuss their research (subject, job, daily routine, peer-review, etc.), helping these future citizens to better understand fundamental research, and to find their bearings by discovering research careers.

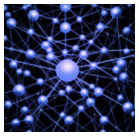
• A documentary film produced by the CNRS, ***"L'hydrogène, futur or vert ?"*** takes us behind the scenes of the H_2 race. This gas has long been at the heart of the work of many French laboratories, which have opened their doors, including ICMPE, with the participation of F. Cuevas, head of the "Interaction of Hydrogen and Matter" group, together with ICARE, FEMTO-ST, IMN, and industrialists such as ALSTOM.

New research projects funded in 2023

• IoTEGH (ANR PRCE) Integrated on chip thermoelectric generator based on Eusler alloys (Moïz, I. Néel), E. Alleno (ICMPE), Coord. D. Tainoff • DoREMI (ANR PRC) Development of new advanced refractory concentrated complex alloys with eutectic carbide/bcc microstructures (IRCP, LSPM, CEMES), Coord. J.-P. Couzinié (ICMPE) • MICS (ANR JCJC) Mixed ion complex hydrides for reversible solid-state hydrogen storage, R. Moury (ICMPE) • ORDERED (ANR PRC) Local structure influence on thermodynamic and kinetic electrochemical properties of Ni-based spinel cathodes (MSME, GeePs, IRCP), Coord. N. Emery (ICMPE) • INFECTION (ANR PRC) AntImicrobial ViruleNce oF MicropattErned SurfaCes in HospiTal EnvIrONment, D.-L. Versace • POLYROSE (ANR PRC) Polyoxometalate-based hybrid materials for antibacterial photodynamic therapy in the visible region, D.-L. Versace.

Upcoming workshops and conferences

• The **annual meeting of the *Groupe Français d'étude des composés d'insertion*** (GFECI), organized by J.P. Pereira-Ramos, R. Baddour-Hadjean, G. Bernari (all 3 at ICMPE), D. Dambournet (PHENIX) and S. Franger (ICMMO), will take place from April 2nd to 5th 2024 in Dourdan. The aim is to bring together the various players involved in insertion compound research, whether academic or industrial.



• The GDR IAMAT will organize thematic days in Grenoble from March 12 to 14, 2024, on the theme of approaches using AI for materials characterization and microstructure description (from experiment or modeling). ICMPE contact: J.-C. Crivello (GDR deputy director).

• The **18th International Symposium on Metal-Hydrogen Systems**, MH2024, will be held in the city of Saint-Malo, French Brittany, on 26 to 31 May 2024. More than 400 researchers will exchange on the fundamental principles of the interaction between hydrogen and matter, and their potential applications. The conference will be co-chaired by Fermin Cuevas (ICMPE) and Yaroslav Filinchuk (UCL, Belgium).

They update their business card

• D. Grande leaves his position as Director of ICMPE to take up the direction of the Charles Sadron Institute (ICS), Université de Strasbourg, as of January 1st, 2024 • J.C. Crivello, head of the Modeling and Calculation group, left ICMPE in August 2023 to join the international unit IRL3629: Laboratory for Innovative Key Materials and Structures (LINK). This Unit is located in Tsukuba, Japan, and it is governed by CNRS, Saint Gobain, and NIMS. ICMPE is a partner unit of LINK • C. Barreteau is the new head of the Modeling and Calculation group of the M2I Department • D. Muller, Assistant Professor at UPEC/ICMPE since 2007, has undergone a new start with her family in the Alps, becoming a secondary school teacher in Grenoble • Y. Cotrebil (BAP B) and S. Penuizic (BAP G) will be promoted Technicien de Classe Exceptionnelle in January 2024 • L. Dammak is the new head of the Bio-M&Ms group of the C3M Department • C. Zlotea (M2I/IHM) has been promoted CNRS Research Director since October 2023 • J. Monnier (M2I/IHM) and J.-G. Malherbe (M2I/MC) have been promoted UPEC Professor of Chemistry and Physics respectively since September 2023 • After ten years as Dean of UPEC's Faculty of Science, J. Moscovici has been appointed UPEC's Defense Security Officer (FSD) since October 2023.

New equipment

Thanks to a UPEC and CNRS co-funding, ICMPE acquired a new liquid-state NMR analyzer for the SPE platform to characterize organic molecules and polymer structures.

Tribute

It was with great sorrow that we learned of the death of our colleague Nicolas Boisseau at the end of the year. Nicolas spent his entire career at CNRS, joining the CECM as an electrician in 1984, and subsequently worked on electrotechnical systems for gamma-ray spectrometry until 2007, and on microcomputing and image processing since then. Nicolas was also a keen ornithologist and wildlife photographer. He put this artistic talent to good use in ICMPE's Graphics Dpt, doing for instance the layouts of ICMPE's NewsLetters. But above all, he was a fun and cheerful colleague who was a pleasure to work with. Our thoughts are with his wife Mireille and to his children Jean-Philippe and Mathieu. Salut Nico !

ICMPE Publication

Publisher: Daniel Grande
Edition: Stéphane Bastide
Design and Print: Loïc Perrière, Julie Bourgon
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