ÉCOLE DOCTORALE
UNIVERSITE BRETAGNE LOIRE
MATIERE MOLECULES ET MATERIAUX

MERCREDI 6 JUIN 2018

9h00 - 17h30

Faculté des Sciences & Techniques
Le Mans Université

INTERVENANT
DR. FABIEN CAPON
UNIVERSITÉ DE LORRAINE
LABCOM VIESSMAN IJL
PRIX YVES ROCARD DE LA SFP

JED 2018
ÉNERGIE, ENVIRONNEMENT

Inscriptions et soumissions des résumés sur le site de la plateforme SciencesConf

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AUX DOCTORANTS EN PHYSIQUE ET CHIMIE
APPARTENANT À L'ÉCOLE DOCTORALE 3M DE L'UNIVERSITÉ BRETAGNE LOIRE

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Contact : jed3m2018@univ-lemans.fr

UNIVERSITE MATIERE
BRETAGNE MOLECULES
LOIRE ET MATERIAUX

Journée de l'Ecole Doctorale

Energie, Environnement

Mercredi 6 Juin 2018

Faculté des Sciences & Techniques

Le Mans Université

Toute l’équipe d’organisation vous souhaite la bienvenue à l’Université du Mans pour cette Journée de l’Ecole Doctorale Matière Molécules et Matériaux sur le thème « Energie, Environnement ». Vous trouverez dans ce fascicule un planning de la journée ainsi qu’une légende concernant les couleurs des badges. Nous nous tenons à votre disposition pour tout problème ou question durant la journée.

Nous vous souhaitons à toutes et à tous une très agréable journée !

L’équipe organisatrice de la JED du Mans 2018

Légende des couleurs de badges :

⬜ Organisation
🟧 Physique
🟩 Physique : Environnement et Biologie
🟪 Physique Subatomique et Instrumentation
🟪 Physique Théorique
🟦 Photonique
🟫 Sciences des Matériaux
🟥 Chimie
🟦 Chimie Inorganique
🟩 Chimie : Procédés et Environnement
🟧 Chimie Physique, Chimie Théorique
🟨 Chimie Moléculaire et Macromoléculaire
🟨 Chimie Analytique et Radiochimie

Planning global :

9h00 – 9h45 :	Salle d’examen	Accueil des participants
9h45 – 10h00 :	Amphi 1	Mot d’accueil
10h00 – 10h45 :	Amphi1	Conférence plénière : Dr. Fabien CAPON
10h45 – 11h00 :	Salle d’examen	Pause
11h00 – 12h30 :	Amphis 1, 2 et 3	Communications orales
12h30 – 14h00 :	Salle d’examen	Pause déjeuner & Session posters
14h00 – 16h00 :	Amphis 1 et 2	Communications orales
16h00 – 16h15 :	Salle d’examen	Pause
16h15 – 17h00 :	Amphi 1	Résultats du sondage, Prix & Clôture
17h00 – 17h30 :		Fin de la journée

Le Mans Université

Plan du campus du Mans

Planning Amphi 1 :

9h45 – 10h00 : Mot d’accueil

10h00 – 10h45 : Conférence plénière : Dr. Fabien CAPON

11h00 – 11h15 : Justine LORTHIOR – Nouvelle architecture de modules photovoltaïques à base de $Cu(In,Ga)Se_2$ – Thématique Physique

11h15 – 11h30 : Yuwei ZHU – Optimizing the photo detection to increase the speed of data acquisition in medical imaging data with 3 photons – Thématique Physique Subatomique et Instrumentation

11h30 – 11h45 : Manel MISSAOUI – Investigation of structural and microstructural properties of $BiFeO_3$ based materials – Thématique Physique

11h45 – 12h00 : Erwann MASSON – Measurement of isolated photons in p-Pb collisions at 5.02 TeV with the ALICE experiment at LHC – Thématique Physique Subatomique et Instrumentation

12h00 – 12h15 : Antony ESCUDIE – Multi-wavelength observation of cosmic-ray air-showers with CODALEMA/EXTASIS – Thématique Physique

12h15 – 12h30 : Yajing XING – The first image of small animal with XEMIS2 and 3γ imaging – Thématique Physique Subatomique et Instrumentation

14h00 – 14h15 : Fanon JULIENNE – Kinetics of polymer degradation and fragmentation in aquatic environment – Thématique Sciences des Matériaux

14h15 – 14h30 : Sylvain LE TONQUESSE – Magnesioreduction : a low temperature synthesis route to CoSb3-based skutterudites with improved thermoelectric properties – Thématique Sciences des Matériaux

14h30 – 14h45 : Emilie EMMANUEL – Toward soil stabilization by alkaline activation of clays – Thématique Sciences des Matériaux

14h45 – 15h00 : Romain GENOIS – Luminescence Tuning by Controlled Reduction of Dopants – Thématique Sciences des Matériaux

15h00 – 15h15 : Marius CESBRON – Bifunctional electrodes obtained by 1,3-dipolar cycloaddition on electrografted azide layer – Thématique Sciences des Matériaux

15h15 – 15h30 : Angélica THOMERE – Wide bandgap photovoltaic chalcogenides : crystal and thin films materials – Thématique Sciences des Matériaux

15h30 – 15h45 : Sacris Jeru TAMBIO – Evaluation of the Electrochemical Performance of Lithium Ion Batteries and Measurement of their Ionic Transport Properties through High Field NMR – Thématique Sciences des Matériaux

15h45 -16h00 : Alfonso FERREIRA – Elastic softness of hybrid lead halide perovskites – Thématique Sciences des Matériaux

16h15 – 17h00 : Résultats du Sondage – Remise des Prix – Clôture de la journée

Conférence plénière

Élaboration en couches minces et caractérisation de matériaux thermochromes pour la régulation thermique

Fabien CAPON[a]

[a] *Institut Jean Lamour (IJL), Université de Lorraine, UMR CNRS 7198, Parc de Saurupt, 54011 NANCY*

La présentation concerne le domaine des capteurs solaires dits thermiques (conversion de l'énergie solaire en chaleur directement exploitable pour la production d'eau chaude). Un laboratoire commun à l'Institut Jean Lamour (UMR 7198 CNRS - Université de Lorraine) et à la société Viessmann Faulquemont SAS, a été crée en 2014. Il a permis le développement, le transfert à l'échelle industrielle, ainsi que la commercialisation de solutions solaires thermiques innovantes récompensés par le Prix Yves Rocard 2016 de la Société Française de Physique. La stratégie de ces recherches est de redynamiser le marché du solaire thermique avec de nouvelles fonctions solaires et plus particulièrement une nouvelle génération de capteurs thermochromes mise sur le marché depuis fin 2016 sous le nom de Vitosol 200 FM. Le capteur intègre une nouvelle couche sélective fonctionnant sur un système vanadium dopé à l'aluminium ThermProtect © permettant la régulation thermique passive du capteur.

Communication orale ☐ ~~**Poster**~~ ☐

New architectures of thin-film photovoltaic modules: towards fully vacuum processes compatible with industrial technologies

Justine LORTHIOIR[a], Nicolas BARREAU[a], Ludovic ARZEL[a]

[a] *Institut des Matériaux Jean Rouxel, Université de Nantes, 44322 NANTES*

In our study, we focus on the structure of the photovoltaic modules based on high-performance Cu(In,Ga)Se_2 thin films. Passing from a solar cell to a photovoltaic module using the current monolithic interconnexion decreases the conversion efficiency about 5% abs. In fact, the architecture of the modules induces optical and resistive losses due to the thick ZnO layer. Additionally the P1 P2 P3 scribings reduce the active area about 10%.

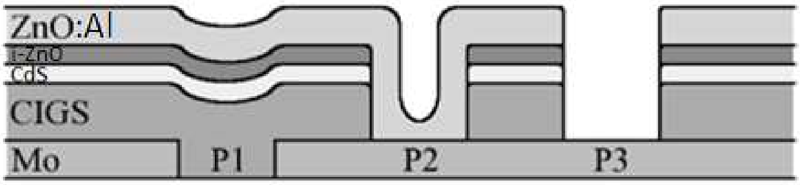

Figure 1 : Standard module with P1 P2 P3 scribings

Thus, we put forward an alternative architecture of modules consisted of a serial interconnexion between cells from the front contact to the back contact directly. For this objective, the Molybdenum (Mo) back contact scribing is carried out using a photolithography process and optimized to minimize the dead zone. Then, the thickness of the thin film layers is also adjusted. This new concept allows to decrease i) the number of scribes, ii) the ZnO thickness, iii) the air exposure of Mo and iv) the inactive area.

Using the same deposition process, we synthesize solar cells and alternative modules consisting of a series of 2 cells. Our preliminary results are very promising and show a high fill factor of 71% for modules and 75% for cells. This suggests a small loss caused by series resistance. A 17% conversion efficiency has been attained for cells while for modules it reached 12%. This decrease may be due to the difference of V_{OC}: 700mV for cells against 1,2V for modules. Further studies, which take these results into account, will need to be performed.

Communication orale ☒ **Poster** ☐

Optimizing the photo detection to increase the speed of data acquisition in medical imaging data with 3 photons

Y. Zhu[a,†], J.M. Abaline[b], S. Acounis[a], N. Beaupère[a], J.L. Beney[a], J. Bert[c]
S. Bouvier[a], P. Briend[d], J. Butterworth[d], T. Carlier[e], H. Chanal[b], M. Cherel[f]
J.P. Cusson-neau[a], M. Dahoumane[g], S. Diglio[a], L. Gallego-Manzano[a]
D. Giovagnoli[c], J. Idier[h], F. Kraeber-Bodere[e], F. Lefèvre[a], O. Lemaire[a]
P. Le Ray[a], S. Manen[b], J. Masbou[a], H. Mathez[g], E. Morteau[a], N. Pillet[b], D. Roy[a]
L. Royer[b], M. Staempflin[d], J.S. Stutzmann[a], R. Vandaele[b], L. Virone[a]
D. Visvikis[c], Y. Xing[a] and D. Thers[a]

[a] *SUBATECH, IMT Atlantique, CNRS/IN2P3, Université de Nantes, 44307 Nantes, France*
[b] *LPC Clermont-Ferrand, 24 Avenue des Landais, Clermont-Ferrand, France*
[c] *INSERM, UMR1101, LaTIM, CHRU Morvan, 2 avenue Foch, Brest, 29600, France*
[d] *AIR LIQUIDE Advanced Technologies Division, F-38360 Sassenage, France*
[e] *Centre Hospitalier Universitaire de Nantes, 1 place Alexis-Ricordeau, 44093 Nantes, France*
[f] *INSERM U892 équipe 13, 8 quai Moncousu, 44000 Nantes, France*
[g] *IPNL Université de Lyon, CNRS/IN2P3 UMR5822, France*
[h] *LS2N, Ecole Centrale de Nantes, CNRS/Inp, Université de Nantes, 44307 Nantes, France*

The XEMIS project (Xenon Medical Imaging System) which makes use of 3γ imaging technique and liquid xenon Compton camera, aims to make a precise 3D localization of a specific radioactive emitter and reducing drastically (100 times less) the injected activity to the patient in cancer diagnosis. The 3γ imaging is based on the detection in coincidence of the two annihilation γ rays and a third high energy γ ray emitted by ^{44}Sc. XEMIS2, which is a larger scale liquid xenon cylindrical camera for small animal imaging, has been designed for preclinical application. The principle of XEMIS2 is based on the measurement of scintillation and ionization signals, which permits to get the position and deposited energy of the interaction between the ionizing particle and the liquid xenon.

This thesis mainly concentrates on the scintillation signal study of XEMIS2. The scintillation signal can firstly provide the γ-rays interaction time, and by matching the scintillation signal with ionization signal, it is possible to reconstruct the Z position with 100 microns accuracy of each interaction point inside the detector. Furthermore, the scintillation signals can be used for spatial pre-localization of γ-ray interactions which aims to increase the efficiency and speed of data acquisition by increasing the activity of the source in XEMIS2.

This presentation will focus on the measurement of scintillation signal in XEMIS2. To detect these signals, the active volume of XEMIS2 is surrounded by 64 UV-sensitive Hamamatsu photomultiplier tubes (PMT) covering 16 sectors in φ. In order to handle the signal from the PMT, a self-triggered scintillation signal detection chain was developed to obtain the interaction time and the duration of the pulse. This chain has been tested and characterized in a prototyping XEMIS1. The result of the first test will be presented. XEMIS2 is now under qualification and the first image of a living small animal is foreseen at the CIMA center of the Nantes Hospital.

Oral communication ☐

Investigation of structural and microstructural properties of $BiFeO_3$ based materials

Manel MISSAOUI [a,b], Maud BARRE[a], Sandrine COSTE[a],
Nirina RANDRIANANTOANDRO[a], Mohamed ELLOUZE[b]

[a] *Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, Le Mans, France.*
[b] *Laboratoire des Matériaux Multifonctionnels et Applications (LaMMA), LR-Physique-Mathématiques et Applications, Université de Sfax, Faculté des Sciences de Sfax(FSS), Route de Soukra km3,5 B.P.1171, 3000 Sfax, Tunisie.*

*Abstract:

Bismuth ferrite ($BiFeO_3$, namely BFO) is the unique perovskite which presents simultaneously ferroelectric ($T_C = 830°C$), ferromagnetic and antiferromagnetic ($T_N = 370°C$) orders at room temperature, so it is called a “multiferroic material”. BFO is stable at this range of temperature, thus it is promising for multifunctional applications such as energy storage and treatment of organic pollutants.

BFO has a modulated cycloïdal spin structure with a long periodicity of 62 nm compared to cell parameters (a_{hex}=0.558 nm, c_{hex}=1.39 nm in the hexagonal symmetry). This distinctive feature is the reason of a very low magnetization ($M_r \approx 0$) resulting in a weak magnetoelectric coupling. Partial substitution of Bi and Fe ions and/or reducing the size of BFO particles are some solutions proposed by different studies in order to suppress this cycloïd and to enhance the magnetic properties. Also it is well known that the range of stability of BFO’s structure in a single phase is very narrow because of the appearance of the secondary phases: $Bi_{25}FeO_{40}$ (sillenite) and $Bi_2Fe_4O_9$ (millite) during the synthesis process[1]. Then, optimizing the preparation conditions is a challenging task to do in order to get a pure compound. This difficulty was reported by the majority of the researches since its discovery on the 70’s, and it is the reason of developing a variety of chemical and physical techniques to overcome this problem and obtain a high performance material.

In this work, we present the results of our essays to substitute BFO powder with non-magnetic compound; and we introduce a new chemical route to produce BFO nanoparticles. The structure and microstructure of those compounds were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

*Key words :

Bismuth ferrite, Multiferroic system, Magnetoelectric coupling, Microstructure, X-ray diffraction.

*Reference :

1. ROJAC Tadej et al. (2014) **$BiFeO_3$ Ceramics: Processing, Electrical, and Electromechanical Properties.** J. American Ceramic Society, pages 1–19.

Communication orale

Measurement of isolated photons in p–Pb collisions at 5.02 TeV with the ALICE experiment at LHC

Erwann MASSON[a]

[a] *Laboratoire SUBATECH, CNRS/IN2P3, Université de Nantes, IMT Atlantique, 44307 NANTES*

Within the Standard Model of particle physics, the behaviour of matter at its fundamental scale is described by Quantum Chromodynamics (QCD). This theory formalises the strong interaction that exists between quarks and gluons, generically referred to as *partons*, and predicts their confinement within hadrons in normal temperature and density conditions. A very energetic context may lead to free the partons from their hadronic structure, resulting in a Quark-Gluon Plasma (QGP) predicted by the QCD theory and experimentally expected in ultrarelativistic heavy-ion collisions such as those provided by the lead-lead (Pb–Pb) system. The ALICE experiment (A Large Ion Collider Experiment) located at the CERN Large Hadron Collider (LHC) can observe such collisions as well as the proton-proton (pp) and proton-lead (p–Pb) systems for which the emergence of a QGP is not predicted, constituting therefore mandatory references to Pb–Pb studies.

In this presentation we are interested in *direct photons* produced at the earliest time of the collision in hard processes between partons, in the case of p–Pb collisions at the centre-of-mass energy of 5.02 TeV. These photons are of particular interest to probe the QCD medium since they escape it without being affected thanks to their insensitivity to the strong interaction. Direct photons must be distinguished from those which are emitted through other channels during the evolution of the system following a collision, especially in parton fragmentation and neutral meson decays (π^0, η, etc.). The photon production mechanisms in hadron collisions will be presented and the way ALICE studies them will be detailed. The emphasis will be put on the measurement of signal related to direct photons and particularly on the way they are isolated from other photon contributions. The first results of this analysis will be presented including the estimation of the underlying event, the isolated direct photon raw spectrum and the purity associated to this signal.

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Communication orale

Multi-wavelength observation of cosmic-ray air-showers with CODALEMA/EXTASIS

Antony ESCUDIE[a]

[a] Laboratoire Subatech, Groupe Astroparticules, UMR 6457, IN2P3/CNRS/IMT Atlantique/Université de Nantes, 4 rue Alfred Kastler, BP20722, 44307 Nantes Cedex 3, France (: antony.escudie@subatech.in2p3.fr)*

Over the years, significant efforts have been devoted to the understanding of the radio emission of extensive air shower (EAS) in the range [20-80] MHz but, despite some studies led until the nineties, the [1-10] MHz band has remained unused for nearly 30 years. At that time it has been measured by some pioneering experiments but also suggested by theoretical calculations that EAS could produce a strong electric field in this band, and that there is possibly a large increase in the amplitude of the radio pulse with lower frequencies. The EXTASIS experiment, located within the radio astronomy observatory of Nançay and supported by the CODALEMA instrument, aims to reinvestigate the [1-10] MHz band, and to study the so-called "Sudden Death" contribution, the expected radiation electric field created by the particles that are stopped upon arrival to the ground. Currently, EXTASIS has confirmed some results obtained by the pioneering experiments, and tends to bring explanations to the other ones, for instance the role of the underlying atmospheric electric field.

Moreover, CODALEMA has demonstrated that in the most commonly used frequency band ([20-80] MHz) the electric field profile of EAS can be well sampled, and contains all the information needed for the reconstruction of EAS: an automatic comparison between the SELFAS3 simulations and data has been developed, allowing us to reconstruct in (quasi-)real time the latter ones. At last, the unique capability of the antennas and acquisition system used in CODALEMA widen the observation window up to 250 MHz. The high-frequency electric field (120-250 MHz) at ground level is expected to be distributed following a ring of amplified emission due to Cherenkov-like effects. We see such patterns in the CODALEMA data which, associated to EXTASIS, allows one to study EAS over a very wide band, from 1 to 250 MHz.

Keywords: cosmic-ray air-showers, radio-detection, CODALEMA/EXTASIS

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LOIRE ET MATERIAUX

Communication orale ☒ **Poster** ☐

The First Image of Small Animal with XEMIS2 and 3γ Imaging

Y. Xing[a,†], J.M. Abaline[b], S. Acounis[a], N. Beaupère[a], J.L. Beney[a], J. Bert[c]
S. Bouvier[a], P. Briend[d], J. Butterworth[d], T. Carlier[e], H. Chanal[b], M. Cherel[f]
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L. Royer[b], M. Staempflin[d], J.S. Stutzmann[a], R. Vandaele[b], L. Virone[a]
D. Visvikis[c], Y. Zhu[a] and D. Thers[a]

[a] *SUBATECH, IMT Atlantique, CNRS/IN2P3, Université de Nantes, 44307 Nantes, France*
[b] *LPC Clermont-Ferrand, 24 Avenue des Landais, Clermont-Ferrand, France*
[c] *INSERM, UMR1101, LaTIM, CHRU Morvan, 2 avenue Foch, Brest, 29600, France*
[d] *AIR LIQUIDE Advanced Technologies Division, F-38360 Sassenage, France*
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[f] *INSERM U892 équipe 13, 8 quai Moncousu, 44000 Nantes, France*
[g] *IPNL Université de Lyon, CNRS/IN2P3 UMR5822, France*
[h] *LS2N, Ecole Centrale de Nantes, CNRS/Inp, Université de Nantes, 44307 Nantes, France*

The 3γ imaging is an innovative functional imaging modality, based on the detection in coincidence of three γ-rays by using on a liquid xenon Compton camera and a (β^+,γ) radionuclide emitter, for purpose of obtaining a 3D image with good precision by using 100 times less activity than in current Positron-emission tomography (PET) systems. A R&D program XEMIS2 dedicated to small animals imaging have been developed to explore the feasibility and advantage of this new application. It's a single-phase liquid xenon cylindrical camera holding around 200kg of liquid xenon, totally surrounding the small animal. The active volume of detector will be covered over with 64 PMTs and two end segmented anodes with a total amount of 20480 pixels, to detect simultaneously the UV scintillation photons and ionization signals, which permits to get the position and deposited energy of the interaction between the ionizing particle and the liquid xenon. In addition, a new self-triggered front-end ASIC for the ionization DAQ chain, XTRACT, have been designed and fabricated with collaboration for the sake of continuous read-out with negligible dead-time during 20 minutes. The expected image quality obtained by a full GATE/Geant4 simulation is very promising with a quite uniform sensitivity throughout the field of view. Now, XEMIS2 is under construction and qualification.

The objective of this thesis is to obtain a high-quality image of small animal with 20 kBq activity during 20 minutes, that greatly dependents on the spatial and energy resolution of detector, the data analysis process and image reconstruction method. In order to optimizing the resolution of detector, the ionization signal should be measured with maximum precision. The ionization signal measurement with the new DAQ chain during testing will be introduced in this presentation.

Communication orale ☐

Kinetics of polymer degradation and fragmentation in aquatic environment

Fanon JULIENNE[a], Nicolas DELORME[a], Taco NICOLAI[a], Christohe CHASSENIEUX[a], Fabienne LAGARDE[a]

[a] *Institut des Molécules et Matériaux du Mans, UMR 6283, Le Mans Université, Avenue Olivier Messiaen 72085Le Mans*

Degradation and fragmentation of non biodegradable polymers in the aquatic environment is a sum of complex phenomena such as photodegradation, thermal oxidation and hydrolysis.[1] Importance of specifics factors such as UV light, temperature, biofouling or polymer formulation is relatively unknown. To provide a better understanding and to predict the evolution of microplastics environmental concentrations, laboratories experimentation are needed. The present study aimed to determine the kinetics of abiotic degradation and fragmentation of polymer as a function of environmental conditions.

Polymer films were machined by blown extrusion to perfectly control their structure and thickness and were placed during several months in an aging chamber under controlled conditions. During all the experiment, the films were regularly analyzed through spectroscopy (UV-visible, IR, Raman) and water contact angle measurements to investigate their kinetics of degradation and of oxidation. SEM and polarized light pictures were also taken to follow the fragmentation. A first insight into the statistical analysis of the size distribution of generated fragments is obtained.

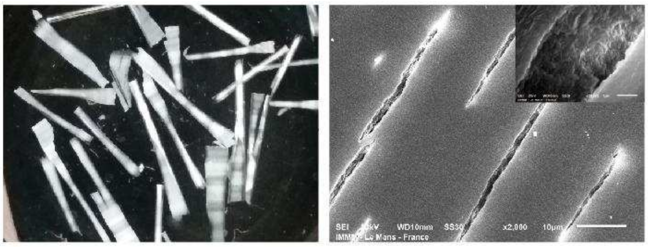

Figure 1: Polarized light and SEM pictures of PE fragments in water

For polyethylene, it appeared that weathering strongly affected all physico-chemical properties (chemical composition, hydrophobicity, crystallinity), and that oxidation occurred as rapidly in water as in air. The number of generated macro-sized fragments did not increase linearly as a function of time, and despite high carbonyl indices, nano-fragments have not been observed in noticeable amount.

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[1] Rajakumar.K et al., (2009) **Natural weathering studies of polypropylene**, Journal of Polymers and the Environment 17, no 3 : 191.

Communication orale

Magnesioreduction: a low temperature synthesis route to CoSb$_3$-based skutterudites with improved thermoelectric properties.

Sylvain LE TONQUESSE [a], Eric ALLENO[b], Valérie DEMANGE[a], Carmelo PRESTIPINO[a], Mathieu PASTUREL[a]

[a] *Univ Rennes, CNRS, Institut des Sciences Chimiques de Rennes, UMR 6226, 35000 Rennes, France*
[b] *Institut de Chimie des Matériaux Paris-Est, CNRS-UPEC UMR 7183, 94320 Thiais, France*

Thermoelectric materials (TM) can directly convert heat into electricity and could be used to partially recover the huge quantity of heat loss in our modern society (car engines, power plants, microprocessors…). Intensive researches are undertaken to improve the currently limited performances of TM which is governed by the figure-of-merit $ZT = \sigma^2T/\rho\kappa$ defined from three intrinsic properties of the materials: the Seebeck coefficient (σ), the electrical resistivity (ρ) and the thermal conductivity (κ). The independent optimization of these properties to maximize ZT is difficult since they are strongly interrelated, almost always limiting the ZT value well below 1.

The skutterudite compound CoSb$_3$ is amongst the most promising TM because nanostructuration and insertion of “rattling” atoms in the structural voids were shown to be efficient strategies to significantly reduce the lattice thermal conductivity without greatly affecting its electronic properties [1]. Together with the optimization of the power factor (σ^2/ρ) by proper doping, these strategies result in ZT above 1.5 in the 750-850 K temperature range.

CoSb$_3$ forms via a peritectic reaction below 1171 K. Its synthesis by conventional fusion-solidification process requires a subsequent annealing (typically 2 weeks long around 1100 K) including intermediate grinding/pelletizing to be brought to completion [2].

In order to save time and energy, magnesiothermic reduction (MTR), which consist in the coreduction of metal oxides by sacrificial magnesium metal, was used as an alternative route to produce pristine, doped and rattler inserted CoSb$_3$ powders. This one-step synthesis has the advantage to be realized in less than 4 days at temperatures as low as 770 K. The powders obtained by MTR are made of well crystallized (sub)micrometric grains which can be readily spark plasma sintered. This presentation will focus on the influence of the key parameters of the MTR process (morphologies/preparation of precursors, reduction temperature range, heat treatment duration), on the structural (XRD) and microstructural (SEM, EBSD) characteristics of skutterudite powders and subsequent improvement of their thermoelectric properties, especially their relatively low thermal conductivity.

[1]SALES B. C. et al. (1996). **Filled Skutterudites: A New Class of Thermoelectric Materials.** Sciences, 1325.
[2]ALLENO E. et al, (2017) **Mesostructured thermoelectric Co$_{1-y}$Ni$_y$Sb$_3$ (M=Ni, Pd) Skutterudite.** J. Alloys Compd., 676.

Communication orale

Toward soil stabilization by alkaline activation of clays

Emilie EMMANUEL[a], Michael PARIS[a], Dimitri DENEELE[a,b]

[a] *Institut des Matériaux Jean Rouxel, Université de Nantes, Nantes*
[b] *IFSTTAR, GERS, EE, F-44344 Bouguenais*

Alkali activation (AA) of metakaolin is considered as one of the most effective way to synthetize geopolymer. This material can display great mechanical properties[1] better than competitive concrete based-OCP (for Ordinary Portland Cement). Its performances are directly linked to the solubility of aluminosilicate source in alkaline solution, depending on the conditions of kaolin calcination. In the context of soil stabilization, a resistance of few megapascals is sufficient to guarantee a good stability over time of the material. In this context, this study aims at assessing the stabilization of model soil rich in kaolins, by alkaline activation at low temperature. Thus, a new way of stabilization, reducing CO_2 emissions and taking into account the soil properties is assessed.

In this work, several alkaline activation ways at low curing temperature (25°C and 40°C) are studied in order to understand the reactivity of kaolinite and its formed products. One of the alkaline activation ways consists of chemical pre-treatments with NaOH at 5 and 10 M in order to improve the dissolution of kaolinite. Then, sodium silicate solution is added to finalize the AA. The evolution of the system is followed using X-ray diffraction (XRD) analysis, ^{29}Si and ^{27}Al NMR, Infrared spectroscopy and scanning electron microscopy in order to describe the formation mechanism of phases.

As expected, the chemical pretreatment, especially at 10M, increases the amount of the kaolin dissolved at the end of the AA process. With chemical pretreatment at 10M, zeolite-type Hydroxysodalite (HS, Si/Al: 1) is identified whatever the pretreatment time (1, 3 or 7 days). In contrast to pretreatment at 10M, the 5M pretreatment resulted in significant changes in the formed products. At 1 day of pretreatment and after 90 days of curing time (after adding sodium silicate solution), an intermediate phase showing ^{29}Si and ^{27}Al NMR signatures similar to geopolymeric signatures is detected. In addition, at 7 days of pretreatment and after 90 days of curing time, a zeolite-type Phillipsite (the most stable zeolite, Si/Al: 2) is also observed by NMR and XRD. The beneficial effect of chemical pretreatment is demonstrated thanks to its capacity to form geopolymer-like phase. However, evaluation of binding properties of the formed products for soil stabilization (zeolites, geopolymers) needs to be conducted.

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Communication orale

Luminescence Tuning by Controlled Reduction of Dopants

Romain GÉNOIS[a], Romain GAUTIER[a]

[a] *Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes cedex 3, France*

The Solid-State Lighting industry, currently estimated at about 26 billion $, is expected to grow to 72 billion $ by 2020. This increase comes from a larger use of Light-Emitting Diodes (LEDs) in every kind of fields (cars, house and public lighting…) leading to energy savings expected at 75% by 2035 [1]. In this context, rare earth-doped phosphors are of great interest for their applications in solid-state lighting. In order to design LEDs with rare earth-based luminescent materials, a few different strategies have been developed. For example, combining blue-emitting InGaN with yellow YAG:Ce^{3+} (YAG = yttrium aluminum garnet) is a widely used approach for WLEDs. However, the white-light emission provided with this method presents low color-rendering index [2]. Codoping the phosphor to tune its color or efficiency is also widely spread [3]. But the impacts on the luminescence properties are hard to predict and every possible dopant cannot be always used. In our work, we developed a new approach to finely tune the luminescent properties of phosphors by "soft" reduction. This technique allows us to control the oxidation state of the dopants leading to different luminescent properties. With this approach, we are able to design precise emission colors for rare earth-doped phosphors such as $SrAl_2O_4$:Eu (figure 1) [4] or Ba_2SiO_4:Eu and to reach single-phase white-light emitting phosphors [5]. Moreover, we extended this method to reach a three-step combinatorial approach, increasing exponentially the discovery speed of phosphors with specific properties.

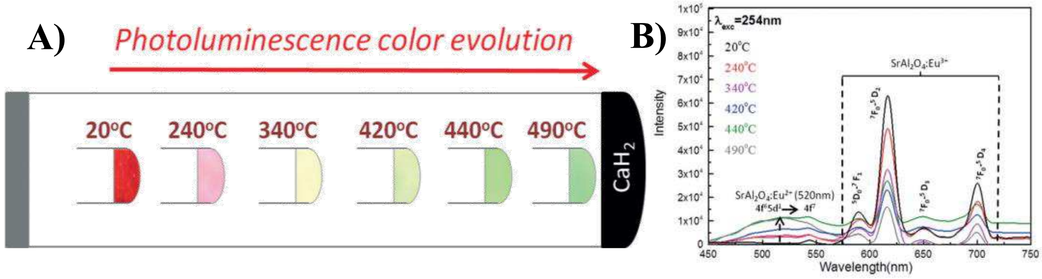

Figure 1: *Photoluminescence color A) and emission spectra B) evolution of* $SrAl_2O_4:Eu^{2+}/Eu^{3+}$ *induced by controlled reduction of dopants.*

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Communication orale

Bifunctional electrodes obtained by 1,3-dipolar cycloaddition on electrografted azide layer

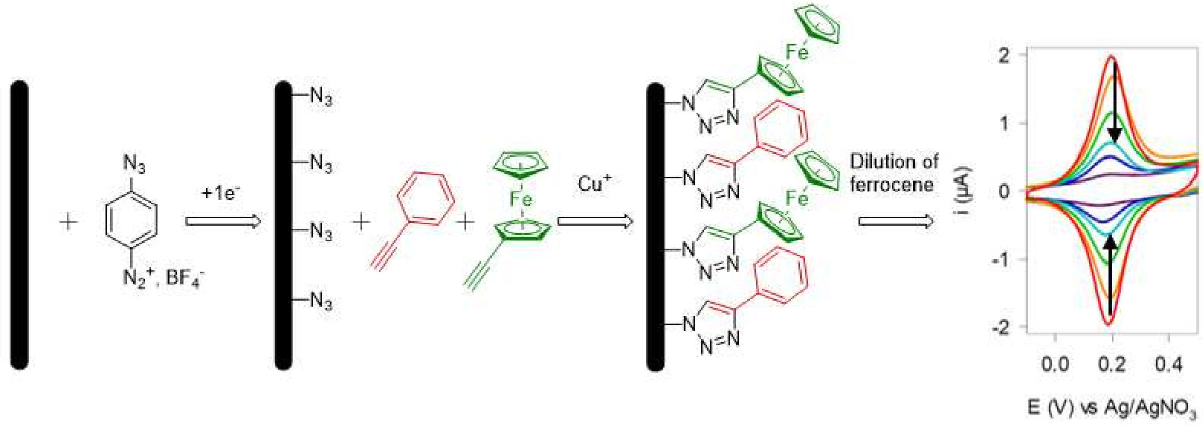
Marius CESBRON[a], Tony BRETON[a], Christelle GAUTIER[a], Eric LEVILLAIN[a]

[a]*Laboratoire MOLTECH-Anjou – UMR 6200 CNRS Université d'Angers, 2 Boulevard Lavoisier, 49045 Angers, France*

Grafting of mixed layers on electrode surfaces allows either the generation of multifunctional or diluted layers[1].

Several strategies have been exploited to obtain robust mixed layers by electrochemical reduction of diazonium salts[2]. Most of the reported works lie on a reduction (simultaneous or successive) of two diazonium salts. However, the control of the grafted functionalities ratio remains challenging and numerous molecular structures are incompatible with this approach. These major drawbacks can be circumvented by the post-functionalization of an active molecular platform.

In the present study, we take advantage of the 1,3-dipolar cycloaddition to form controlled binary organic films from an azido platform obtained reduction of 4-azidobenzenediazonium [Schema 1]. Electrochemistry and XPS studies on modified films have shown a clear impact of the ethynyl derivative structure on the final ratio obtained on surface.



Schema 1. Mixed layer obtained by post-functionalization.

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Communication orale / ~~Poster~~

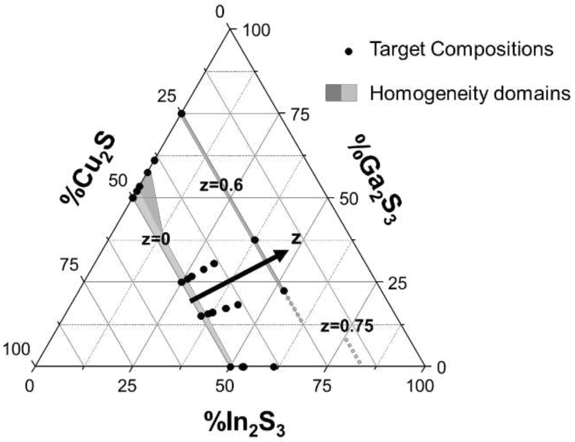
Wide bandgap photovoltaic chalcogenides : crystal and thin films materials

Angélica THOMERE[a,b,c], Catherine GUILLOT-DEUDON[a], Nicolas BARREAU[a], Romain BODEUX [b,c], Marie-Therese CALDES[a], Alain LAFOND[a]

[a] *Institut des Matériaux Jean Rouxel (IMN), UMR 6502 CNRS, Université de Nantes, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France*
[b] *EDF R&D, 30 Route Départementale 128, 91120, Palaiseau, France*
[c] *Institut Photovoltaïque d'Ile-de-France (IPVF), 30, Route départementale 128, 91120 Palaiseau, France*

With the aim to overcome the theoretical efficiency of single junction solar cell of 30%, tandem cells involving two cells have been proposed. Chalcopyrite such as Cu(In,Ga)S_2 (CIGS) can be used as the top cell with a silicon-based bottom cell if its bandgap is about 1.7eV. The selenides counterparts (Cu(In,Ga)Se_2) are well known to give rise to solar cells with high efficiency but the sulphides are investigated because sulphur is less expensive, less toxic and more abundant than selenium[1]. Here, we present the chemical crystallographic structural investigations of CIGS compounds on powders, crystals and thin films. We paid specific attention to existence of the so-called Cu-poor compounds because of the crucial role they play in solar cells.

First, stoichiometric powders and single crystals of $Cu(In_{1-x}Ga_x)S_2$ have been studied and the classical chalcopyrite structure (*I*-42*d*) for these compounds was confirmed[2]. Afterwards, Cu deficiencies were introduced (see Figure). A two phase domain appeared in the Ga-free compounds, $Cu_{1-z}In_{1-z/3}S_2$, with a stoichiometric phase $CuInS_2$ and a Cu-poor one $Cu_{0.25}In_{1.25}S_2$ ($CuIn_5S_8$) with a thiospinel structure *F*-43*m*. When Ga is added, another Cu-poor phase appeared in $Cu_{1-z}(In,Ga)_{1-z/3}S_2$ with an hexagonal structure and a composition $Cu_{0.40}(In,Ga)_{1.2}S_2$ ($Cu(In,Ga)_3S_5$). The corresponding Cu-poor phase $CuGa_3S_5$ has a tetragonal structure *I*-42*m*. Finally a ternary diagram of composition is proposed for the bulk (see Figure) for the Cu_2S-In_2S_3-Ga_2S_3 system. It remains that the chalcopyrite structure is not kept when Cu content is decreased.



Cationic substitutions are checked in order to stabilize the structure with copper-deficiencies. Additionally, thin films are deposited by coevaporation in order to establish a link between the properties of the bulk and the film: film constraints could involve new phases. The first solar cells have also been prepared and give promising results.

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Communication orale

Evaluation of the Electrochemical Perfromance of Lithium Ion Batteries and the Measurement of their Ionic Transport Properties through High Field NMR

Sacris Jeru TAMBIO[a], Michaël DESCHAMPS[b], Vincent SAROU-KANIAN[b], Aurélien ETIEMBLE[c], Thierry DOUILLARD[d], Eric MAIRE[d], Bernard LESTRIEZ[a]

[a] Institut des Molécules et Matériaux Jean Rouxel, UMR 6502 CNRS, 2 rue de le Houssiniere, Nante, France
[b] CEMHTI Orléans, 1 Avenue de la Recherche Scientifique, 45100 Orléans, France
[c] Institut Jean Lamour, CNRS UMR 7198, Université de Lorraine, 54011 Nancy Cedex, France
[d] Univ Lyon, INSA Lyon, CNRS, MATEIS, UMR 5510, F-69621 Villeurbanne, France.

ANR project PEPITE aims to tailor electrodes for lithium-ion batteries for electronic vehicles. The limitation of lithium ion battery's application in electric automobiles stems from both slow charge and discharge rates. These processes are highly dictated by the diffusion of the lithium ion in the porous matrix [1]. A multi-pronged approached was conceptualized which combine multiple characterization techniques. This study focuses on the use of Pulsed Field Gradient – Spin Echo NMR (PFG-SE NMR), electrochemical cycling and FIB-SEM imaging to map out electrode morphology and its effects on lithium ion diffusion.

Magic-Angle Spinning, Pulsed Field Gradient, Stimulated-Echo Nuclear Magnetic Resonance (MAS-PFG-SE NMR) was used to measure self-diffusion coefficients of LP30 electrolyte species for the first time in model composites. These composite electrodes were made of alumina, carbon black and PVdF-HFP. Alumina's magnetic susceptibility is close to the measured magnetic susceptibility of the LP30 electrolyte thereby limiting undesirable internal field gradients [2]. Interestingly, the self-diffusion coefficient of lithium ions decreases with increasing carbon content. FIB-SEM was used to describe the 3D geometry of the samples. The comparison between the reduction of self-diffusion coefficients as measured by PFG-NMR and as geometrically derived from FIB/SEM tortuosity values highlights the contribution of specific interactions at the material/electrolyte interface on the lithium transport properties.

Keywords
Lithium ion battery, diffusion, Nuclear Magnetic Resonance (NMR), Magic Angle Spinning (MAS), Pulsed Field Gradient (PFG)

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Communication Orale

Elastic softness of hybrid lead halide perovskites

Afonso FERREIRA[a,b], Antoine LÉTOUBLON[b], Serge PAOFAI[c], Stephane RAYMOND[d], Claude ECOLIVET[e], Benoit RUFFLÉ[f], Stephane CORDIER[c], Claudine KATAN[c], Makhsud SAIDAMINOV[g], Ayan ZHUMEKENOV[g], Osman BAKR[g], Jacky EVEN[b] and Philippe BOURGES[a]

[a] *Laboratoire Léon Brillouin, CEA-CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France*
[b] *Laboratoire FOTON, INSA, Université Rennes, F35708 Rennes, France*
[c] *Institut des Sciences Chimiques de Rennes, CNRS, Université de Rennes 1, Ecole Nationale Supérieure de Chimie de Rennes, INSA de Rennes, 35042 Rennes, France*
[d] *Univ. Grenoble Alpes, CEA, INAC, MEM, 38000 Grenoble, France*
[e] *Institut de Physique de Rennes, CNRS, Université de Rennes 1, 35042 Rennes, France*
[f] *Laboratoire Charles Coulomb, UMR 5221, Université de Montpellier, 34095 Montpellier, France*
[g] *King Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center, KAUST Solar Center, Physical Sciences and Engineering Division (PSE), Thuwal 23955-6900, Saudi Arabia*

Hybrid organic-inorganic perovskites (HOP) have been intensively studied as promising materials for photovoltaic applications, taking advantage of their high efficiency and low cost processing. Although much recent attention has also been devoted towards unraveling their microscopic optoelectronic properties, the origin of their softness, by comparison to classic semiconductors, is currently still lacking a comprehensive understanding and systematic experimental studies. Here we investigate by coherent inelastic neutron scattering spectroscopy and Brillouin light scattering, low frequency acoustic phonons in four different hybrid perovskite single crystals: $MAPbBr_3$, $FAPbBr_3$, $MAPbI_3$ and α-$FAPbI_3$. We report a very small shear C_{44} elastic constant for all the compounds and a considerable elastic anisotropy. The extremely low bulk modulus and negative C_{12} in α-$FAPbI_3$ substantiates its very unstable nature and in $FAPbBr_3$, a tendency towards an incipient ferroelastic transition, is interpreted as further evidence of the influence of plasticity in hybrid perovskites. We observe a systematic lower sound group velocity in the technologically important iodide-based compounds compared to the bromide-based ones. The findings suggest that low thermal conductivity and hot phonon bottleneck phenomena are expected to be enhanced by low elastic stiffness, particularly in the case of the ultrasoft α-$FAPbI_3$. This project has received funding from the European Union’s Horizon 2020 programme, through a FET Open research and innovation action under the grant agreement No 687008.

Planning Amphi 2 :

11h00 – 11h15 : Marie BICHON – Aqueous Processing of Cathodes for Li-Ion Batteries – Thématique Chimie : Procédés et Environnement

11h15 – 11h30 : Jessica FLORES GONZALEZ – Isotopes to drive Lanthanide Single-Molecule Magnets – Thématique Chime Moléculaire et Macromoléculaire

11h30 – 11h45 : Amirhossein HABIBI – Push-pull molecules as donor materials for Organic solar cells – Thématique Chimie Moléculaire et Macromoléculaire

11h45 – 12h00 : Sathya NARAYANASAMY – Influence of glass composition on vapor hydration of nuclear waste glasses – Thématique Chimie

12h00 – 12h15 : Tran Nu Thanh Viet BUI – Rheology and microstructure of mixture of iota and kappa-carrageenan in presence of potassium ions – Thématique Chimie Moléculaire et Macromoléculaire

12h15 – 12h30 : Maroua BEN HAJ SALAH – Halogenated perovskites for PeLEDs applications – Thématique Chimie Inorganique

14h00 – 14h15 : Nataliya PLYUTA – Coordination chemistry of Schiff base ligands based on 2,1,3-benzothiadiarole – Thématique Chimie Moléculaire et Macromoléculaire

14h15 – 14h30 : Mehdi TAZI – Ferrocene : the future is in my lab – Thématique Chimie

14h30 – 14h45 : Clémence NICOLAS – New polydicyclopentadiene-based crosslinked material for use in extreme conditions – Thématique Chimie Moléculaire et Macromoléculaire

14h45 – 15h00 : Antonin LEBLANC – Lead and iodide deficient $(CH_3NH_3)PbI_3$, d-MAPI : the bridge between 2D and 3D hybrid perovskites – Thématique Chimie

15h00 – 15h15 : Yaoyin LOU – Preparation of Ni Coated Graphite Felt Modified Ag Nanoparticles for Dechlorination of Chlorinated Compounds – Thématique Chimie : Procédés et Environnement

15h15 – 15h30 : Kévin LEMOINE – Synthesis of mixed-cations oxyfluorides as positive electrode for lithium secondary batteries – Thématique Chimie Inorganique

15h30 – 15h45 : Youssef AIDIBI – Development of multi-modal and multi-level molecular systems – Thématique Chimie Moléculaire et Macromoléculaire

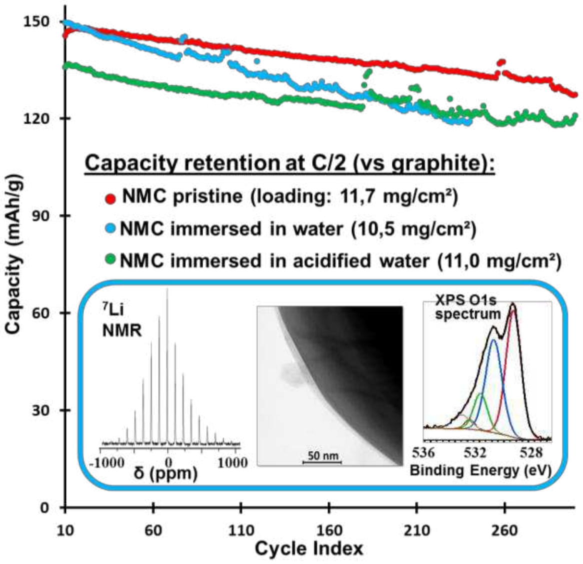
15h45 -16h00 : Margaux LHUISSIER – Absorption of volatile organic compounds in waste oils – Thématique Chimie : Procédés et Environnement

Communication orale ☒ / Poster ☐

Aqueous Processing of Cathodes for Li-Ion Batteries

Marie BICHON[a], Adrien BOULINEAU[a], Eric DE VITO[a], Nicolas DUPRE[b], Dane SOTTA[a], Willy PORCHER[a], Bernard LESTRIEZ[b]

[a] *CEA Liten, 17 rue des Martyrs, 38054 Grenoble Cedex 9*
[b] *Institut des Matériaux Jean Rouxel, CNRS UMR 6502, Université de Nantes, 2 rue de la Houssinière, 44322 Nantes Cedex 3*



Lithium-ion batteries, which are widely used in portable electronics, are also considered as the most promising technology to power electric vehicles. In this regard, recent studies have focused on increasing their energy density, especially by developing new cathode materials[1]. Nickel manganese cobalt layered oxides (NMC) with high amount of nickel are one of these high density materials.

The conventional preparation of positive electrode requires the use of N-Methyl-2-pyrrolidone (NMP), which is a toxic solvent. In order to reduce the cost and environmental impact of the cathode manufacturing process, a recent approach consists in replacing the NMP solvent with water[2].

This study aims at evaluating the effect of such water-based process on the electrochemical performances of the cathode. One of the main issues to be addressed when processing Ni-rich powders in aqueous slurries is related to the surface modification of the material. Lithium ions can be leached out from the particle, forming a resistive layer of lithium carbonate and hydroxide[3]. These species are also responsible for the alkaline pH of the slurry, which might cause corrosion of the aluminum collector[4]. Addition of acid to the slurry is often used to lower the pH and avoid this corrosion. To understand the phenomena occurring when processing Ni-rich materials in an aqueous slurry, qualitative and quantitative analysis were carried out on NMC 532 powders after immersion in pure or acidified water. Ion leaching was evaluated by ICP-OES measurements. TEM analysis revealed chemical and structural evolution at the surface. Amount of surface impurities such as hydroxides and carbonates was also determined using ^{7}Li MAS NMR and pH titration. Additionally, XPS measurements were carried out to clarify the nature of the amorphous layer formed at the surface of the particles. Electrodes prepared using NMP, water or acidified water as solvent were cycled in half and full cells to assess the effect of surface evolution on the electrochemical performances.

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Communication orale ☐

Isotopes to drive Lanthanide Single-Molecule Magnets

Jessica FLORES GONZALEZ,[a] Lahcene OUAHAB,[a] Fabrice POINTILLART*[a] & Olivier CADOR *[a]

[a] *Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS - Université de Rennes 1*
263 Avenue du Général Leclerc 35042 Rennes Cedex (France)

Lanthanides play an important role in the field of molecular magnetism. Complexes based on these trivalent cations possess strong magnetic anisotropy and high magnetic moment, crucial for enhancing the energy barrier and therefore displaying a slow relaxation of their magnetization and magnetic hysteresis at low temperature, which are the properties making them interesting for their use as Single-Molecule Magnets (SMMs).[1]

In the group two different lanthanide ions (Dy^{III} and Er^{III}) have been used in order to study the importance of the contribution of intermolecular (dipole) and intramolecular (hyperfine) interactions on the magnetic relaxation, and to play with both contributions to tune their performances. On one side, dysprosium is mainly constituted by four stable isotopes with different nuclear spin ^{161}Dy and ^{163}Dy, with I=5/2, and ^{162}Dy and ^{164}Dy, with I=0. A Dy^{III}-based mononuclear complex has been synthesised and two different strategies applied: 1) isotopic enrichment in order to play with the hyperfine interactions, and 2) magnetic dilution to isolate the molecule from the neighbouring complexes.[2,3] On the other side, erbium is constituted by six stable isotopes, mostly with I=0, with the exception of $^{167}Er^{III}$ with I=7/2. In that case, an Er^{III}-polyoxometallate complex of literature[4,5] has been synthesized in order to study the isotopic effect on the relaxation of the magnetic moment.

A full dynamic study of the magnetic response for both complexes has been carried out and the different results have been compared in order to distinguish any difference while changing from an oblate electronic distribution (Dy^{III}) to a prolate one (Er^{III}).

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Communication orale

Push-pull molecules as donor materials for Organic solar cells

Amir Hossein HABIBI, Olivier SEGUT, Martin BLAIS, Pierre JOSSE, Olivier ALEVEQUE, Clément CABANETOS, Jean RONCALI, Philippe BLANCHARD

MOLTECH-Anjou, UMR CNRS 6200, University of Angers, 2 Boulevard Lavoisier, 49045 Angers, France

Organic solar cells (OSCs) have attracted increasing research interest in the last decade, due to their potential low cost, lightweight, fast fabrication and flexibility in comparison with the traditional silicon-based solar cells. OSCs have been subjected to constant improvements either by developing new organic materials and/or by optimizing their architecture and their processing conditions, leading recently to power conversion efficiencies (PCEs) up to 15%.[1] Typically, conventional OSCs are made from an electron-donor and an electron-acceptor materials sandwiched between a transparent Indium Tin Oxide (ITO) electrode with high work function and a low work function metallic electrode *e.g.* in aluminum. Although impressive results on non-fullerene acceptors have very recently given renewed interest to OSCs, fullerene derivatives have been widely used as electron-acceptors in Organic Photovoltaics (OPV). On the other hand, π-conjugated polymers and small molecules are usually utilized as donor materials, the later showing a discrete structure allowing for more accurate structure-properties relationships, reproducible synthesis and properties, and an easier purification.

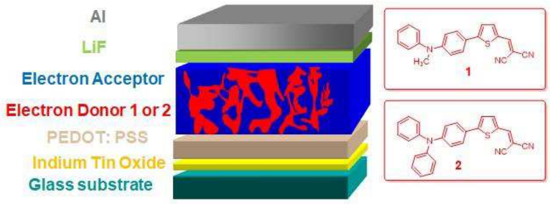

Figure 1- Architecture of a BHJ OSC and structure of push-pull molecules **1** and **2**.

Small D-π-A push-pull molecules represent an interesting class of molecular donors for OPV because of their strong absorption in the visible spectrum and their synthetic accessibility.[2,3] In this context, we present here a revisited synthesis of push-pull molecule **1**[4] and compare the photovoltaic performance of bilayers OSCs using C_{60} or C_{70} as acceptor materials. In addition bulk heterojunction OSCs (Fig. 1) based on the push-pull molecules **1** or **2** as donors and soluble fullerene derivatives $PC_{60}BM$ and $PC_{70}BM$ as acceptors, will be described and characterized. Thus the photovoltaic performance have optimized by developing new device architectures (bilayer *vs* bulk heterojunction), optimizing the processing conditions (solution *vs* vacuum, thermal annealing), controlling the thickness of the photoactive layers and changing the nature of the acceptor. The impact of these parameters on the photovoltaic performance of OSCs based on push-pull molecule **1** and **2** will be presented.

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Communication oral☐

Influence of glass composition on vapor hydration of nuclear waste glasses

Sathya NARAYANASAMY[a], Patrick JOLLIVET[a], Frédéric ANGELI[a], Nicole GODON[a], Abdesselam ABDELOUAS[b], Florent TOCINO[c], Hélène SCHNEIDER[c]

[a] *CEA Marcoule, DEN, MAR, DE2D, SEVT, LCLT, Bât 208, BP 17171, 30207 Bagnols/Cèze cedex, France*
[b] *SUBATECH, CNRS-IN2P3, IMT Atlantique-Université de Nantes, 4 rue Alfred Kastler, BP 20722, 44307 Nantes cedex 03, France*
[c] *EDF-R&D, Matériaux et Mécanique des Composants, EDF Lab. Les Renardières, 77818 Moret Sur Loing cedex, France*

High activity and intermediate activity radioactive waste that are principally produced by nuclear power plants are concentrated and confined in a vitreous matrix. ANDRA, the French national radioactive waste management agency, is studying a project of a deep geological repository for disposal of these nuclear waste glass matrices poured in stainless steel canisters and surrounded by non-alloy steel overpacks. It is considered that after a few thousand years, during the overpack corrosion, the radioactive glass could be exposed to unsaturated medium for tens of thousands of years before groundwater saturates the repository [1]. Consequently, the effects of temperature, relative humidity (RH) and pH of the atmosphere on the vapor hydration of various French nuclear waste glasses have been studied [2].

The aim of the thesis is to study the influence of the glass composition on vapor hydration kinetics and mechanisms. In this framework, three complex glasses (>20 oxides) from a series of glass compositions called AVM (*Atelier de Vitrification de Marcoule*) and three simplified glasses (Q, QCa, QMg) containing 4 or 5 oxides were chosen for the study. These glasses permitted to study the specific influence of Ca and Mg in comparison to the Q glass that contains 4 oxides (Si, B, Na, Al). Monoliths of the six glasses were altered in a climatic chamber at 50°C and 95% RH for six months. The hydration kinetics was followed using FTIR spectroscopy. After six months of hydration, the glass samples were characterized using SEM/TEM/XRD/ToF-SIMS. The evolution of the FTIR spectra over six months shows a notable effect of glass composition on hydration kinetics. The SEM images show that the glass with the thickest hydrated glass layer has the largest quantity of precipitated secondary phases at the surface. Two of the complex glasses also have an irregular thickness of the hydrated layer where the thickness is a few hundreds of nm in certain zones and a few µm in other zones that are probably below a surface precipitate. Small quantities of secondary phase precipitates are visible even for glasses that have been altered to a relatively lesser extent. These results indicate that the hydration of AVM glasses is most likely driven by the precipitation of secondary phases. The ToF-SIMS profiles of element behavior in the hydrated layer relative to the pristine glass have shown a detrimental effect of Ca and Mg on vapor hydration. Although the three complex glasses have similar composition with different stoichiometry, the difference in their hydration rates suggests a significant effect of stoichiometry on glass hydration.

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Oral Communication

Rheology and microstructure of mixture of iota and kappa-carrageenan in presence of potassium ions

Viet T.N.T. BUI[a], Fréderic RENOU[a], Bach T. NGUYEN[b], Taco NICOLAI[a]
[a]Polymères, Colloïdes et Interfaces, UMR CNRS 6283, Le Mans Université, 72085 Le Mans cedex 9, France.
[b]Food Technology Faculty, Nha Trang University, Nha Trang city, Vietnam

We will discuss the rheological properties and microstructure of native kappa carrageenan (κ-car), iota carrageenan (ι-car) and their mixtures in the presence of KCl. For both pure and mixed solution, increasing the KCl between 5 and 100 mM increased the elastic modulus (G_{el}) and the gelling temperature (T_g). Further increase of the KCl concentration did not led to an increasing of the elasticity. In addition, a artefact occurred with κ-car added excess KCl. However, this phenomenon had not seen in mixed systems even at high salt concentration, 100 mM. The elastic modulus of the mixtures at low temperatures was much higher than the sum of those of the pure systems within the same conditions.

In parallel, the influence KCl on the structure of pure and mixed gels was studied by confocal laser scanning microscopy (CLSM). In the mixtures, κ-car and ι-car could be distinguished because they were covalently labelled with different fluorescent dyes. CLSM images show that ι-car is distributed more homogeneously than κ-car both in pure gels and in the mixtures. The structure of κ-car and ι-car in the mixtures was found to be different to each other indicating that the two polysaccharides were not fully co-located as shown in figure 1. Furthermore, the mobility of each carrageenan in pure and mixed systems was evaluated by Fluorescence Recovery After Photobleaching (FRAP). The results shown that the mobility of car in pure systems were quicker than in mixed system at the same polymer concentration. The results on Light Scattering supported to the synergistic in κ-car/ ι-car gels.

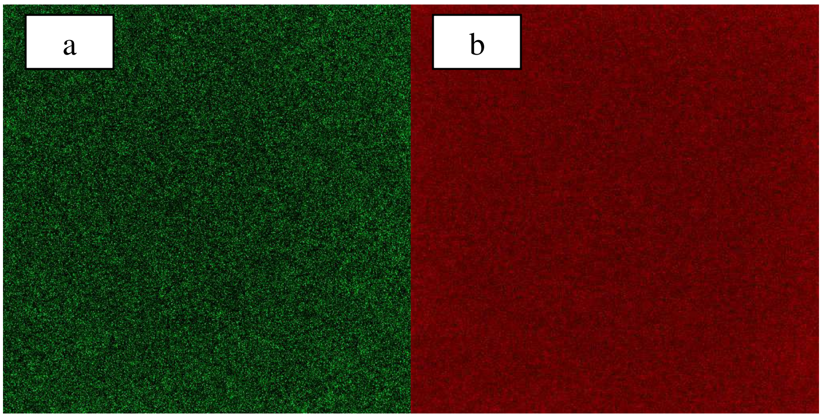

Fig 1: CLSM images of mixed gels containing 10 g/L κ-car and 10 g/L ι-car with 50 mM KCl. The signal of labelled κ-car is shown in (a) and the signal of labelled ι-car is shown in (b).

HALOGENATED PEROVSKITES FOR PeLEDS APPLICATIONS

Maroua BEN HAJ SALAH [a], Nicolas MERCIER [a], Antonin LEBLANC [a]
Magali ALLAIN [a], Chiara BOTTA [b]

[a] MOLTECH-Anjou,UMR-CNRS6200,University of Angers ,Angers,France
[b] ISMAC,CNR,University of Milan,Milano,Italy.

Since less than 10 years and the first report on the 3D hybrid perovskite (HP) $(CH_3NH_3)PbI_3$ as sensitized material in a solar cell[1], The recent contribution of our group to this field is the discovery of a new family of hybrid perovskite, dubbed d-HPs, $(MA,HEA)_{1+x}[Pb_{1-x}I_{3-x}]$ ($0.10 \leq x \leq 0.20$) (MA^+ methylammonium, HEA^+ hydroxyethylammonium), which combine a reduced lead content and an improved stability compared to MAPI.[2] Besides photovoltaics, $(A)PbX_3$ HPs nanocrystals have received great attention recently due to their potential application in the fabrication of very efficient light emission devices (PeLEDs for Perovskite LEDs). Depending on the halide composition (X= I, Br, Cl or mixed Cl/Br, Br/I), the emission can be tuned in the all visible range.[3] Moreover, the potentiality of intrinsic white-light emission by layered bromo- and chloro-plumbate HPs (2Ds) have been recently showed.[4]

In this communication, we report the results of our effort to prepare new materials for PeLEDS applications:

1- A family of 2D HPs $(CO_2H\text{-}(CH_2)_{n-1}\text{-}NH_3)_2Pb(X,X')_4$ (X= Br, Cl) exhibiting white luminescence with Photo Luminescence Quantum Efficiency (PLQE) reaching 15% which constitutes a record;
2- A series of four hybrids materials based on 1D perovskite networks $Pb_nBr_{(4n+2)}^{(2n+2)-}$ with n= 2, 3, 4, 5, allowing to establish property (luminescence)-structure relationships for hybrid perovskites whose network varies from 1D to 2D ($n= \infty$);
3- Highly luminescent properties of nanocrystals of the lead and bromide deficient $(CH_3NH_3)PbBr_3$ compound, $(MA,HEA)_{1+x}[Pb_{1-x}Br_{3-x}]$.

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Communication orale ☐

Coordination chemistry of Schiff base ligands based on 2,1,3-benzothiadiazole

Nataliya PLYUTA[a,b], Svitlana PETRUSENKO[b], Vladimir KOKOZAY[b],
Thomas CAUCHY [a] and Narcis AVARVARI[a]

a MOLTECH-Anjou Laboratory CNRS-UMR 6200, University of Angers, 2 bd. Lavoisier, 49045 ANGERS, France

b Department of Inorganic Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska str. 64/13, Kyiv 01601, Ukraine

nataliya.plyuta@etud.univ-angers.fr

Nowadays, one of the most popular ligands are Schiff base ligand, which are easily synthesized and modified. Their metal complexes are continuing to attract the attention due to their wide range of applications (including catalysts, medicine, magnetism, anti-corrosion agent, crystal engineering).[1] The increasing interest in homo- and heterometallic complexes in various fields has stimulated the design of ligands able to accommodate a pre-established number of metal ions. Compounds bearing 2,1,3-benzothiadiazole have received much attention because of their potential use in fluorescent materials, fungicides, antibacterials, plant growth and protection and gene regulation, organic conductors and molecular recognition.[2] 2,3,1-Benzothiadiazole is one of the most important ring in the chemistry of luminescent compounds. We have been interested in looking at coordination properties for Schiff base ligands with the 2,3,1-benzothiadiazole moiety.
Herein we present the syntheses and characterisations of Schiff bases ligands (HL^1 and HL^2), which are products of condensation of 4-amino-2,1,3-benzothiadiazole and salicylic aldehyde (HL^1) or *ortho*-vanillin (HL^2). Transition metal and lanthanide complexes such as $[Cu(L^1)(Hfac)]$, $Co(L^1)_2$, $Ni(L^1)_2$, $Zn(L^1)_2$ and $Cu(L^2)$ $[Zn(L^2)_2(HL^2)]$, $[Nd(HL^2)_2(NO_3)_3]$ were obtained and crystal structures of all these compounds were determined by X-ray analysis.

Funding and acknowledgement: Embassy of France in Ukraine, University of Angers, Laboratory Moltech-Anjou.

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Communication orale

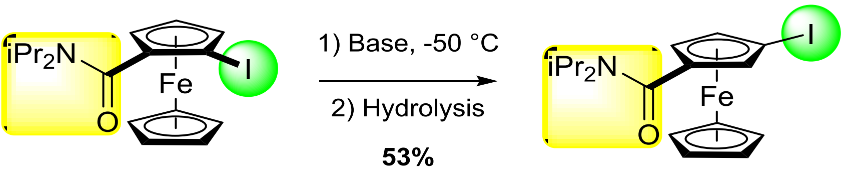
Ferrocene: the future is in my lab

Mehdi TAZI,[a] Yuri S. HALAUKO,[b] Oleg A. IVASHKEVICH,[b] Vadim E. MATULIS,[c] Thierry ROISNEL,[a] Vincent DORCET,[a] William ERB[a] and Florence MONGIN[a]

[a] *Univ Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France.*
[b] *UNESCO Chair of Belarusian State University, 14 Leningradskaya Str., Minsk 220030, Belarus*
[c] *Research Institute for Physico-Chemical Problems of Belarusian State University, 14 Leningradskaya Str., Minsk 220030, Belarus.*
mehdi.tazi@univ-rennes1.fr

The discovery of ferrocene by Keally, Pauson and Miller in 1951 rejuvenated organometallic chemistry with the emergence of metallocene chemistry.[1] Due to their specific properties (three dimensional structure, redox behavior and high stability), ferrocene derivatives have found various applications as catalysts, fuel additive, polymers and even promising drugs, showing their impact in our everyday life.[2] However, these developments remain limited to specific classes of ferrocene derivatives (monosubstituted, 1,1'- or 1,2-disubstituted), almost excluding 1,3-disubstituted derivatives. This results from the lack of easy and general syntheses of these derivatives.

Here, we will describe the development of a three steps synthesis of these original derivatives, based on the halogen 'dance' reaction, an isomerization process well known in the benzene series.[3] Through the careful choice of substituents and reaction conditions (nature and amount of product, temperature, reaction time), we managed to develop the first efficient and practical halogen 'dance' reaction in the ferrocene series.[4] The original derivatives were further functionalized to highlight their interest.



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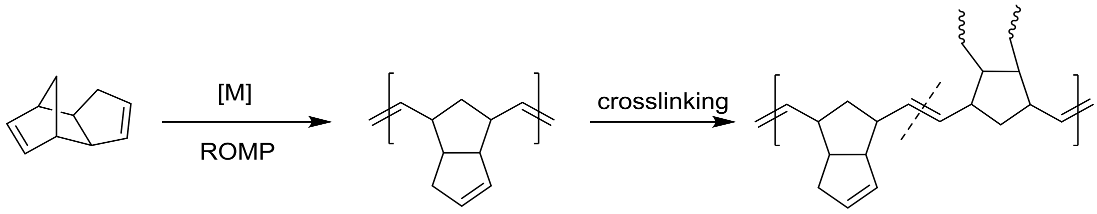
Communication orale

New polydicyclopentadiene-based crosslinked materials for use in extreme conditions

Clémence Nicolas, Véronique Montembault, Laurent Fontaine

Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, Le Mans

Decrease oil reserves and global increase in oil demand are extending the economic viability of deep-sea oil extraction. However, the extreme conditions of extraction require materials with compatible mechanical properties and chemical resistance. In particular, a polymer coating to ensure thermal insulation of steel pipes and to avoid over-cooling of the oil is necessary. Crosslinked polydicyclopentadiene (PDCPD) (Scheme 1) shows good potential for this application [1, 2]: it is a good thermal insulation polymer, it has a high impact resistance, a good resistance to chemical corrosion and a high heat deflection temperature. Moreover, PDCPD has economical interest: the feedstock of its monomer dicyclopentadiene (DCPD) is abundant [2] and its polymerization by ROMP (Ring-Opening Metathesis Polymerization) does not need heat. However, the use of this polymer in applications presenting high environmental risks needs to improve its ageing properties. Indeed, PDCPD oxidized faster than hydrocarbon polymers, such as polyethylene, despite a lower concentration of double bonds [3] due to catalyst residues.



Scheme 1: Structure of crosslinked polydicylopentadiene

In this context, this project deals with the improvement of the chemical stability of crosslinked PDCPD by limiting oxidation. Two strategies are studied:
-copolymerization of DCPD with functional comonomer bearing antioxidant functions,
-introduction of (co-)polymers synthetized from antioxidant-functionalized monomers as additives into PDCPD.

In this communication, the synthesis of antioxidant-functionalized monomers synthesis, their homopolymerization and copolymerization with DCPD by ROMP is presented. This research is supported by ANR VRPOM n° ANR-15-CE08-0025.

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Communication orale

Lead and iodide deficient $(CH_3NH_3)PbI_3$, *d*-MAPI: the bridge between 2D and 3D hybrid perovskites

Antonin LEBLANC, Nicolas MERCIER*[a], Magali ALLAIN[a], Jens DITTMER[b], Vincent FERNANDEZ[c], Thierry PAUPORTE*[d]

[a] *MOLTECH ANJOU, UMR-CNRS 6200, Université d'Angers, 2 Bd Lavoisier, 49045 Angers, France.*
[b] *Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS,, Avenue Olivier Messiaen, Le Mans.*
[c] *Institut des Matériaux Jean Rouxel, UMR 6502, Université de Nantes, 2 rue de la Houssinière, 44322 Nantes.*
[d] *Chimie ParisTech, Institut de Recherche de Chimie Paris (IRCP), 11 rue P. et M. Curie Paris..*

The last years, the Hybrid Perovskite based solar cells (PSCs) showed a high photoconversion efficiency (PCE) up to 22,7%.[1] The best performances were obtained with the three-dimensional $CH_3NH_3PbI_3$ and derivatives such as mixed small cations and mixed halogens $(Rb,Cs,FA,MA)PbI_{(3-x)}Br_{(x)}$ compounds, where MA^+=methylammonium and FA^+=formamidinium.[2]

Very recently, we have discovered a new family of hybrid perovskites, named *d-MAPI*, which can be prepared as single crystals, crystallized powders and crystallized thin films. A *d-MAPI* phase is lead and iodide deficient compared to MAPI ($CH_3NH_3PbI_3$): a $(PbI)^+$ unit being substituted by an organic monocation, while keeping a 3D architecture. By using two kinds of organic cations, the methylammonium and the ethanolammonium (HEA^+), a series of *d-MAPI* compounds whose general formulation is $(MA)_{1-2.48x}(HEA)_{3.48x}[Pb_{1-x}I_{3-x}]$ ($0<x<0.20$) has been obtained. The substitution of $(PbI)^+$ unit leads to the formation of channels along c axis. Channels of this network can be filled by extra Pb^{2+} and I^- ions and organic cations (when $x<0.20$) or only by organic cations (when $x= 0.20$). First experiments using *d-MAPI* layers for an application as absorber materials in regular FTO/compact-TiO2/meso-TiO2/Perovskite/SpiroOMeTAD/Ag PSCs have shown that *d-MAPI* ($x= 0.10$) exhibits a PCE of 6%. Moreover, a relative stability test of thins films of MAPI and *d-MAPI* ($x= 0.10$) has revealed that *d-MAPI* thin films are more stable than the MAPI ones. This new type of hybrid perovskite $(A,A')_{1+x}[Pb_{1-x}Y_{3-x}]$ ($A= MA^+$, $A'= HEA^+$) offers increased flexibility of its chemical composition with potential substitutions on the A, A', Pb and Y sites.

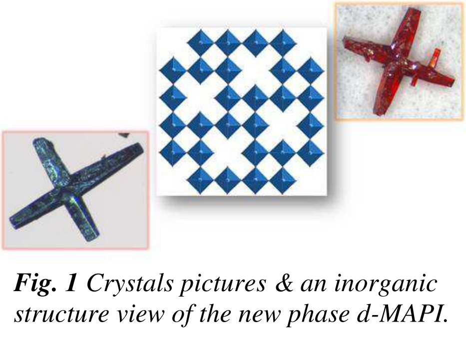

***Fig. 1** Crystals pictures & an inorganic structure view of the new phase d-MAPI.*

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Communication orale

Preparation of ni coated graphite felt modified ag nanoparticles for dechlorination of chlorinated compounds

Yaoyin LOU,[a,b] Wenyan He,[a,b] Florence Fourcade,[b]
Abdeltif Amrane,[b] Florence Geneste[a]

a Université de Rennes 1, ISCR, UMR-CNRS 6226, Equipe Matière Condensée et Systèmes Electroactifs
b Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France

Alachlor has been one of the mostly used herbicide to remove annual grasses and broadleaf weeds and promote crops yield, in the last few decades. But the excess use of alachlor led to contaminations in surface water and farming soil. Alachlor and some of its metabolites have been detected in vitro in human liver microsomes and in urine. Electroreduction process has been proposed as one alternative for the removal of hazardous organic halides without the need of extra chemicals and with the whole process performed in mild conditions. It has been proved that Ag possesses good electrocatalytic ability regarding on cleavage of the C-Cl bond at low cathodic potential with a high removal yield [1]. Nanoscale Ag can decrease the manufactural cost of the cathode, when dealing with a large volume of water, and can enhance the electrocatalytic performance by high surface/volume ratio, compared to the polycrystalline bulk counterpart.

Recently, we have selected nickel covered graphite felt (Ni@GF) and Ni foam as electrode supports owning to their very good electronic conductivity, good mechanical resistance, and large void volume fraction to improve mass transfer [2]. Nano-Ag modified 3D electrodes, Ag-PVP-Ni@GF and Ag-PVP-Ni foam, were developed for dechlorination of organic chlorides in aqueous solution. Nano-Ag was spontaneously deposited on the two 3D supports by galvanic displacement reaction since it is easy to perform and scale-up as it does not suffer from inhomogeneous current distribution. PVP was used as a capping agent to control the shape and the size of nano-Ag. Ag loading was found to be 7.2 times higher in Ag-PVP-Ni@GF than in Ag-PVP-Ni foam. Average particle size of nano-Ag in Ag-PVP-Ni@GF (40 nm) was smaller than in Ag-PVP-Ni foam (107 nm) (Figure 1). The electrochemical active surface area of Ag-PVP-Ni@GF was around 3 times higher than that of Ag-PVP-Ni foam.

Ag-PVP-Ni@GF (0.1335 cm^3) exhibited the highest catalytic activity toward the dechlorination of 50 mg/L alachlor at -0.9 V/MSE, with a conversion yield of 98% in 0.05 M NaOH after 100 min and current efficiency up to 37%. The yield of the main dehalogenated product, deschloroalachlor, was over 70%.

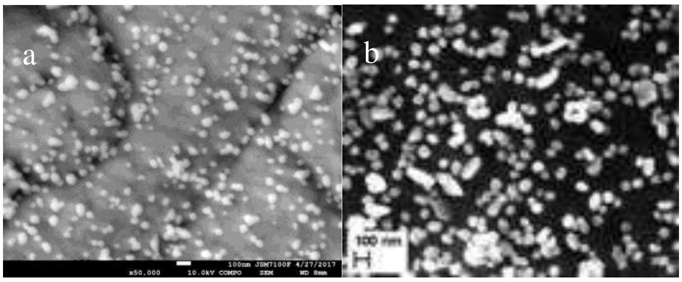

Figure 1: SEM images of Ag-PVP-Ni@GF (a) and Ag-PVP-Ni foam (b)

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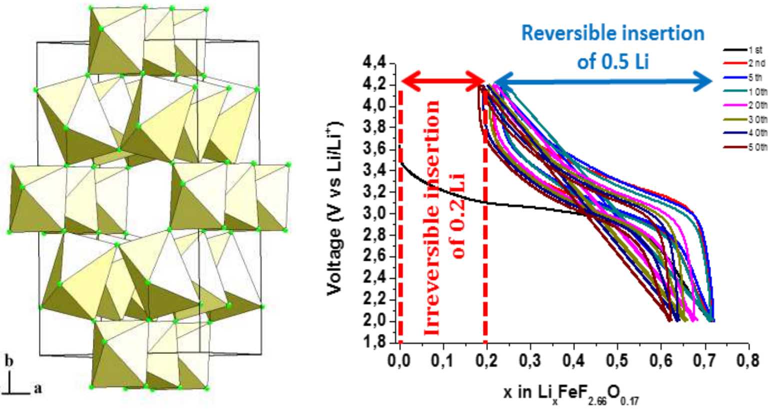
Communication orale ☐

Synthesis of mixed-cations oxyfluorides as positive electrode for lithium secondary batteries

Kevin LEMOINE[a], Jérôme LHOSTE[a], Annie HEMON-RIBAUD[a],
Marc LEBLANC[a], Jean-Marc GRENECHE[a],
Jean-Marie TARASCON[b], Vincent MAISONNEUVE[a]

[a] *Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, Le Mans*
[b] *Chimie du Solide-Energie, UMR 8260, Collège de France, 11 Place Berthelot, 75231 Paris Cedex 05*

In the last decades, fluoride materials have attracted attention as cathode materials for secondary batteries; the high electronegativity of fluoride affords higher potentials in comparison with oxides [1]. The applicably of fluorides as cathode materials was demonstrated with carbon fluorides CF_x for Li-Ion primary Batteries (LIB) in the 80's and the study of metal fluorides started around 2005. Two allotropic varieties of iron fluorides adopt open-framework structures which are favourable for alkaline ion insertion: Hexagonal Tungsten Bronze (HTB) with 1D tunnels and pyrochlore with 3D interconnected tunnels.
The aim of my work is to identify new positive electrode fluoride materials for LIB .The study relates to previously known fluorides that were not tested in electrochemistry such as the series of inorganic transition metal fluorides $MM'_2F_8(H_2O)_2$ and their derivatives obtained by dehydration [2]. Several compounds combining various M^{+II}/M^{+III} couples were synthesized by a solvothermal route assisted by microwave heating. The oxyfluoride $FeF_{2.66}O_{1/6}$ with the HTB structural type, obtained by dehydration of $Fe_3F_8(H_2O)_2$, exhibits a significant electrochemical activity with a reversible capacity of 120 mAh.g^{-1}.



Representation of the HTB structure (left); Cyclic voltammetry curves at 20 mA.g^{-1} for $FeF_{2.66}O_{1/6}\square_{1/6}$ obtained by dehydration of $Fe_3F_8(H_2O)_2$ (right).

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Communication orale

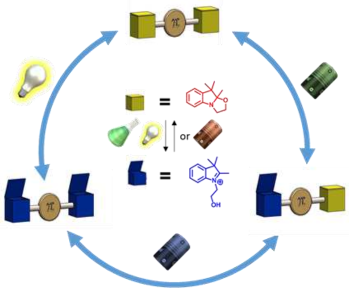
Development of multi-modal and multi-level molecular systems.

Youssef AIDIBI,[a] Clement GUERRIN,[b] Philippe LERICHE,[a] Stephanie DELBAERE,[b] Lionel SANGUINET[a]

[a] *Laboratoire MOLTECH Anjou (UMR 6200) Université d'Angers 2, bd Lavoisier 49045 ANGERS Cedex – France*

[b] *UMR CNRS 8516, LASIR Equipe "Photophysique, Réactivité et Fonctionnalité" Service de Physique et de RMN Faculté des Sciences Pharmaceutiques et BiologiquesUniversité de Lille, UDSL3, rue du Professeur LaguesseBP 83, 59006 LILLE cedex, France*

Over the past decade many efforts have been focused on the synthesis, modification and application of multi-responsive molecular systems[1]. Up to now, two main strategies have been conducted to elaborate such systems: either by connecting different molecular switches through covalent links[1, 2] or by mixing them within supramolecular assemblies to obtain multi-responsiveness through the combination of various stimulations (*i.e.*, photon, electron, proton, magnetic field, etc…). In this communication, we present a different approach based on the employment of indolinooxazolidine (BOX) unit as multi-modal switch. Indeed, the opening of the oxazolidine ring can be reversibly and selectively achieved either under UV irradiation, electrochemical stimulation or acidity changes. Moreover, the connection of two of them around a central pi conjugated core should lead to an enhancement of the number of available metastable states and allow the modulation of a property over several discrete levels.Nevertheless, the selective addressability of each subunit is still a quite challenging task in multi-switch system. Within this context, we want to take advantage of the existence of interactions through the bonds between both BOX units to assure their differentiation over some stimulation. Indeed, acido-, photo- and electro-chromic properties of the BOX units are not affected in an identical manner and lead to their global (referenced as all-in mode) or partial (referenced as stepwise mode) switch depending on the nature of the stimulation (see figure 1).For this study, we have prepared and explored the multimodal switching features of a first series of compounds which integrates a simple 2D aromatic plate forms, such as bithiophene, and EDOT-Thiophene-EDOT unit as spacer between the two BOX units, allowing to tune the redox potential of the system. Going further, in order to promote the metastable states, we tried to increase the number of BOX by connecting three of them on more elaborated pi systems, such as tris (4-(thiophen-2- yl) phenyl) amine (TPA) and by playing on the arms of it. As supported by the performed spectroscopic characterizations, the acidic stimulation leads to global opening of BOX units in a successive manner. At the opposite, electrochemical stimulation assure a better control of the number of commutated BOX unit due to a strong variation of the redox potential with the oxazolidine ring opening.



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Communication orale

Absorption of volatile organic compounds in waste oils

Margaux LHUISSIER[a,b], *Abdoulaye KANE*[c], *Abdeltif AMRANE*[a], *Jean-Luc AUDIC*[a], *Annabelle COUVERT*[a]

[a] ENSCR, UMR CNRS 6226, 11 Allée de Beaulieu – CS 50837, 35708 Rennes, France

[b] CHIMIREC, 20 Z.I. de Mézaubert, 35133 Javené, France

[c] *EME,* Campus de Ker Lann, 35170 Bruz, France

Volatile organic compounds (VOC) are air pollutants causing health and environmental problems. At low concentration in waste gas they can be removed in bioreactors, but this technique shows a questionable efficiency when treating hydrophobic VOC. An option for their removal is to combine their absorption in an organic solvent and their biodegradation in a two-phase partitioning bioreactor in order to regenerate the scrubbing liquid. In previous studies, silicone oil proved to be an effective solvent towards toluene[1].However, the cost of such a solvent is not negligible, and an alternative could be to use waste oils.

To fulfill the required specifications, the oil must present several characteristics, such as low or no volatility (to avoid VOC stripping during operation), low viscosity (to limit pressure drop during operation), excellent affinity for target VOC (conditioning the performances of the absorption step). Then, the purpose of this study was to realize a screening of several waste oils in order to find the most suitable for the whole process. Consequently, partition coefficients of 5 waste industrial oils and 8 different VOC were measured at T=25°C. Besides, the volatility of these oils was evaluated, before and after water washing. Then, the performances of two of these oils, selected according to their affinity and volatility results, were measured in a packed column filled with Flexipac structured packing.

As expected, hydrophobic VOC show more affinity towards oils than hydrophilic VOC. Moreover, the tested waste oils show similar performances in terms of absorption. Volatility experiments reveal that except for waste engine oil, the oils emit VOC at a concentration widely lower than the air threshold, i.e. 110 mg m^{-3} total carbon, which is further lowered by water-washing. Finally, based on cost and availability, two oils were chosen for column essays, which are still in progress.

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Planning Amphi 3 :

11h00 – 11h15 : Chaimae EL FAKIR – Thermal infrared active hyperspectral imaging – Thématique Photonique

11h15 – 11h30 : Yahaya HASSAN LONI – Temporal uranium record of oak tree rings (Quercus petrae) by (LA)-HR-ICP-MS from a former uranium mining site (Rophin, France) – Thématique Chimie Analytique et Radiochimie

11h30 – 11h45 : Maureen DENIEL – Spectroscopiy tools characterisation of an environmental problematic : Nanoplastic-microalgae interaction – Thématique Physique : Environnement et biologie

11h45 – 12h00 : Ghina HAJJAR – Food authentication using isotopic and metabolomic NMR of lipids – Thématique Chimie Analytique et Radiochimie

12h00 – 12h15 : Anh Dung NGUYEN – Mechanical properties of Red Blodd Cell membranes probed with the Circular Mode Atomic Force Microscopy – Thématique Physique : Environnement et biologie

Communication orale

Thermal infrared active hyperspectral imaging

Chaimae El Fakir[a], Luiz Poffo[a], Bastien Billiot[b], Pascal Besnard[a], Jean-Marc Goujon[a]

[a] Univ Rennes, CNRS, Institut FOTON – UMR 6082, F-22300 Lannion, France
[b] AII-CMI, 35400 Saint-Malo, France

Analysis of chemical composition, structure, quality of area and temperature of materials or biological elements, allows characterization and diagnostic of materials. This analysis is usually carried out by two techniques: spectroscopy or imaging. Spectroscopy aims to determine the composition and chemical structure of sample by identifying atomic and molecular vibration, while imaging is widely applied to study the spatial distribution of these components. The combination of these two techniques in the multispectral (disjoint spectral bands) and hyperspectral (continuous bands) imaging allows to extract simultaneously the spectral and spatial signatures related to the structure and physiology of sample.

We propose some architectures of active multi or hyperspectral imaging in thermal band (3-14 µm) shown in figure 1, allowing to associate with observation system an artificial optical source with controlled spectrum. In the first architecture (figure 1-a), the sample is excited by broad band thermal source, the transmitted or reflected wave is then filtered in wavelengths and collected by imager. While for the second architecture (figure 1-b), filters are positioned before sample.

The recent availability of the tunable laser QCL (Quantum Cascade Laser) allows us to propose hyperspectral architecture as described in figure 1-c, illuminating the sample by a tunable narrow spectrum source. Reflected or transmitted radiation is then collected by standard thermal imager.

In order to evaluate more precisely the capacities of the proposed system, we have developed an experimental bench, allowing to determine the variations of spectral reflection and transmission of materials.

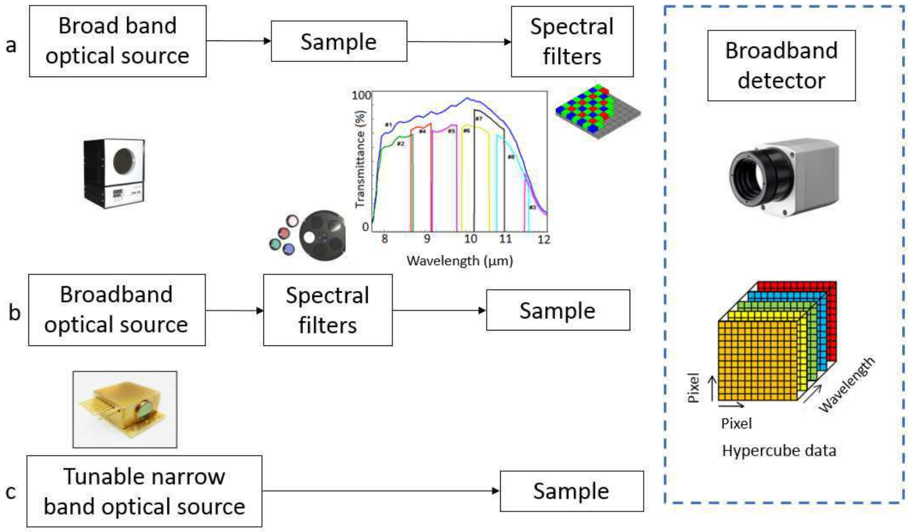

Fig. 1: Three architecture examples for multi or hyperspectral active imaging.

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Communication orale

Temporal uranium records of oak tree rings (*Quercus petrae*) by (LA)-HR-ICP-MS from a former uranium mining site (Rophin, France)

Y. HASSAN LONI[a], K. DAVID[a], S. LARRUE[b], G. MONTAVON[a], P. CHARDON[c], B. GRAMBOW[a]

[a] *Laboratoire SUBATECH, Groupe Radiochimie, UMR 6457, IN2P3/CNRS/IMT Atlantique/Université de Nantes, 4, rue Alfred Kastler, 44000 Nantes Cedex 3, France*
[b] *GEOLAB, UMR 6042, CNRS/Université Clermont Auvergne, 4, rue Ledru, 63057 Clermont-Ferrand Cedex, France*
[c] *LPC, UMR 6533, IN2P3/CNRS/Université Clermont Auvergne, 4, avenue Blaise Pascal TSA60026 CS60026, 63178 Aubière Cedex, France*

The site of Rophin (Puy de Dôme, France) was used for uranium mining between 1949 and 1958. About 30 tons of uranium were extracted and 30,000 tons of wastes were stored on the ground afterwards. The aim of the study is to use oak tree rings as biomonitors of past and recent uranium contamination from mining activities in order to contribute to a better characterization of uranium transport.
Tree-ring samples were taken on six 150 years old oaks trees (*Quercus Petraea*) closely located upstream and downstream (with respect to the hydrologic system) of the site where uranium was mined and which is actually used for residue storing.
High Resolution Inductively Coupled Plasma Mass Spectrometry (HR-ICP-MS) was used to analyze concentration traces of U within the tree-rings with both laser ablation (LA) and solution modes. Time resolved uranium signals were normalized to ^{13}C internal standard signals and various materials were used for quantification. Two-dimensional (2D) mapping of uranium allowed to study U spatial distribution at 1 mm² surface of tree rings. A strong heterogeneity was observed, with U concentration ranging from 1 to 50 ppb. This leads to average U concentrations with high 1σ uncertainties (40-60%). In addition, comparison with U analyses performed in solution highlighted the limitation of the LA technique. Thus, the solution mode was selected. Annual rings were analyzed for the year 1900 (i.e. before mining), 1940, 1952 and 1958 (during mining) and 1990 (during the rehabilitation period). According to the geochemical background, our findings showed an increase in concentration varying between 1 to 45 ppb for the trees located downstream of the mining site and thus supporting an U mobility in the past. Moreover, the results are consistent with the presence of a marked wet area located close to the trees.

Communication orale

Spectroscopy tools : characterisation of an environmental problematic : Nanoplastic-microalgae interaction

Maureen DÉNIEL[a], Aurore CARUSO[b], Fabienne LAGARDE[a], Nicolas ERRIEN[a]

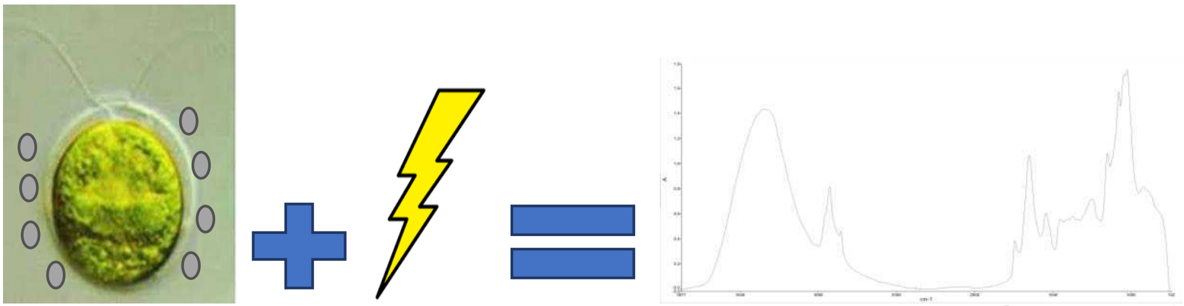
[a] *IMMM -UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, Le Mans*
[b] *Laboratoire Mer, Molécules, Santé, EA 2160, Le Mans Université, Avenue Olivier Messiaen, Le Mans*

In context of environmental change, particles pollution, is more and more studied notably plastic. Some authors suggested that plastic can be found in nanoparticle state[1]. Nanoparticles can have others proprieties than the initial material and detection of little debris is complex due to their size.

Moreover, importance of understand their potential toxicity on organisms is relieved in literature[2]. Impact on organisms like microalgae can lead to trophic transfert.

This work tends to present interest of infrared microspectroscopy to study nanoplastic-microalgae interaction. This technic provide possibility to indirectly detect this particles by study chemical composition of microalgae.

Results of this interaction was monitored with infrared spectroscopy and also with classical biology method (growth, enzymatic assay, genes expression by quantitative polymerase chain reaction). No significant toxic effect of nanopolystyrene on *Chlamydomonas reinhardtii* was revealed. However, variation of lipids/proteins and nucleic acid/proteins ratio was observed with statistical analysis of infrared spectra.



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Communication orale

Food authentication using isotopic and metabolomic NMR of lipids

Ghina HAJJAR[a,b], Toufic RIZK[b], Joseph BEJJANI[b], Serge AKOKA[a],

[a] *EBSI team, Interdisciplinary Chemistry: Synthesis, Analysis, Modelling (CEISAM), University of Nantes-CNRS UMR 6230, 2 rue de la Houssinière, BP 92208, F-44322 Nantes cedex 3, France*
[b] *Laboratory of Metrology and Isotopic Fractionation, Research Unit: Technologies et Valorisation Agroalimentaire (TVA), Faculty of Science, Saint-Joseph University of Beirut, P.O. Box 17-5208 Mar Mikhael, Beirut 1104 2020, Lebanon*

Food industry is a fertile ground for fraud and adulteration. NMR emerged as a powerful analytical tool for food authentication. It is used for metabolomic analysis and position-specific isotopic measurements of target molecules, such as lipids. Their isotopic fingerprint and metabolomic profile are influenced by the geographical and botanical or animal origins of the matrix, weather conditions, and, in the case of products of animal origin, the animal's nutrition. In a previous work, Lebanese olive oils were classified according to their sub-regional origins using proton[1] and carbon-13[2] NMR of triglycerides. The aim of the present work is to be able to use other lipid fractions, such as cholesterol and phospholipids, in order to avail of the complete isotopomic profile of the lipid fraction. In this respect, egg yolk was chosen as a model matrix, being rich in lipids.

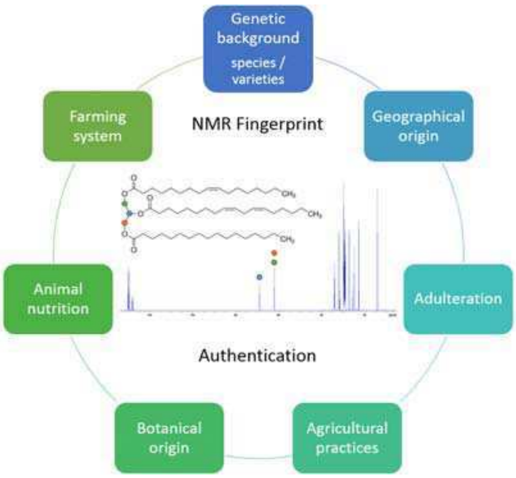

Fig. 1: Factors affecting the metabolic profile and the isotopic composition of target molecules.

The extraction procedure was optimized to avoid isotopic fractionation and to permit a precision (per mil) required for isotopic ^{13}C-NMR. Egg samples from different Lebanese traditional and industrial farms were collected, and triglycerides, phospholipids, and cholesterol were isolated. The pulse sequence (adiabatic INEPT sequence[3]) and deconvolution procedure of ^{13}C-NMR spectra were optimized in order to reach the desired high precision. ^{13}C-NMR spectra were recorded on a 500 MHz spectrometer, and peak areas were obtained from curve fitting, carried out in accordance with a Lorentzian-Gaussian mathematical model using at least five parameters for each peak: position, height, linewidth, phase and Gaussian-to-Lorentzian ratio. The determined peak areas were used as descriptors in the construction of multivariate models for the classification of egg samples according to their origin or to the corresponding farming system.

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Oral Communication

Mechanical properties of Red Blood Cell membranes probed with the Circular Mode Atomic Force Microscopy

Anh Dung NGUYEN

Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, Le Mans

The principle of the Circular Mode Atomic Force Microscopy (CM-AFM)[1] consists in imposing a constant and continuous high frequency circular lateral displacement to the AFM tip in the plane of the investigated system. By using a lock-in amplifier, it is possible to measure the amplitude and the phase of the main harmonic of the lateral force signal in quasi-stationary conditions. With CM-AFM, the relative lateral circular displacement of the probe can be combined with a vertical displacement, i.e. with the force spectroscopy mode, widely used for the study of biological systems (see for example, punch through experiments[2]). Hence, the friction law (i.e. the lateral force vs. the normal force) and the indentation/adhesion force (i.e. the vertical approach/retract force curves) are instantaneously and simultaneously measured. For Life sciences, the originality of CM-AFM is the lateral stress of the biological specimen (eventually combine to normal stress) at high sliding velocities allowing determining, simultaneously and instantaneously, physical properties in a single procedure and thus, giving access to behaviors and properties that are impossible to obtain with conventional AFM modes such as imaging or force spectroscopy modes.

In our study, we have modified the composition of red blood cell membranes by applying a specific nutritional protocol based on micro-algae and omega 3. Our measurements with the CM-AFM show that it is possible to differentiate the molecular heterogeneity of the cell membranes by probing their surface properties.

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Liste des Posters :

1 - José María ANDRES CASTAN *Chimie Moléculaire et Macromoléculaire*
Novel push-pull molecules based on N-methyl-N-phenylthiophen-2-amine as organic donors for organic solar cells

2 - Khryslyn ARANO *Sciences des Matériaux*
Li-ion Batteries with High Energy Density Based on Silicon and Ionic Liquid. Towards All Solid Devices.

3 - Debashish BANERJEE *Chimie Analytique et Radiochimie*
Effect of small organic molecules on the adsorption and transport of radionuclides in clay materials: From Molecular Modeling to Environmental Fate!

4 - Yohan CHERET *Chimie Moléculaire et Macromoléculaire*
Multifunctional ligands based on TTF-Triphenylamine-Terpyridine: synthesis and complexation studies

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6 - Emmelyne CUZA *Chimie Inorganique*
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7 - Florian DAMAS *Physique Subatomique et Instrumentation*
Integration of the ALICE muon spectrometer geometry in the O_2 software

8 - Lionel DOMERGUE *Chimie : Procédés et Environnement*
Study of the scale-up electrochemical reactor with a fixed bed three-dimensional cathode for the degradation by electro-Fenton with the Fe-EDDS complex of persistent pollutants in the water

9 - Walid EL AYED *Sciences des Matériaux*
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11 - Manuel GUITTIERE *Physique Subatomique et Instrumentation*
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12 - Hadi HACHEM *Sciences des Matériaux*
Towards highly conducting metal bis-dithiolene complexes

13 - Ahmad HOBBALLAH *Chimie*
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14 - Xavier INSOU *Photonique*
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15 - Meriem KEMEL *Photonique*
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Eco-friendly and fast synthesis of polypyrrole and reduced grapheme oxide foam nanocomposite and its application to supercapacitors

17 - Erwann LE COZ *Chimie*
Synthesis of the first Barium Boroxide complexes and application in dehydrocoupling

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Synthesis of amphiphilic copolymers applied to the crystallization of calcium carbonate particles in supercritical CO_2 by a continuous and eco-friendly emulsification process

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30 - Chloé THERREAU *Physique*

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31 - Elodie VASQUEZ *Sciences des Matériaux*

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32 - Pauline VERITE *Chimie Physique, Chimie Théorique*

Theoretical study of the excited state intramolecular proton transfer (ESIPT) of highly emissive organic dyes

33 - Karolina WASZKOWSKA *Physique*

Diagnostic of linear and nonlinear optical properties of some specific metallo-supramolecular thin films based on triple helicates

34 - Jianhan XIONG *Sciences des Matériaux*

Formulation and characterization of silicon-based electrodes for high energy density Li-ion batteries

Poster

Novel push-pull molecules based on *N*-methyl-*N*-phenylthiophen-2-amine as organic donors for organic solar cells

José María ANRES-CASTAN, Pablo SIMON-MARQUES, Clément CABANETOS, Philippe BLANCHARD

MOLTECH-Anjou, UMR CNRS 6200, University of Angers, 2 Boulevard Lavoisier, 49045 Angers, France.

josemaria.andrescastan@univ-angers.fr

Nowadays, organic solar cells (OSCs) have received increasing attention due to their advantages in comparison to silicon-based solar cells, such as lower manufacturing cost, lightweight and flexibility. The photoactive layer of these cells is usually composed of an electron-donor and an electron-acceptor placed between a transparent electrode with high work function and a low work function metallic electrode. Their structure and composition have been subjected to constant modifications in an attempt to improve their final performance.

Push-pull conjugated molecules D-π-A, where D and A are an electron-donating and an electron-accepting blocks respectively, represent one type of electron-donor materials that allows obtaining good photovoltaic performances. Among others, push-pull molecules based on triphenylamine (TPA) stand out due to its strong electron-donating properties and high hole-mobility.[1] In addition, this TPA structure is quite tunable since its modification can deeply affect the optical, electrochemical and photovoltaic properties.[2-3] Regarding this fact, we present a novel electron-donating block based on *N*-methyl-*N*-phenylthiophen-2-amine which will be combined with different π-spacers and electron-accepting blocks (Fig. 1). The electrochemical and optical properties of the resulting molecules, as well as their photovoltaic performance, will be discussed in relation to the nature of (i) the π-spacer and (ii) the electron-accepting block.

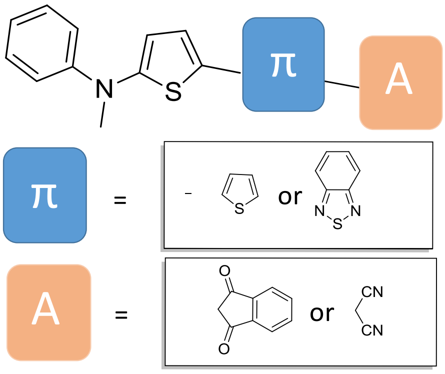

Figure 1. General structure of the push-pull molecules synthesized.

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Communication Poster

Li-ion Batteries with High Energy Density Based on Silicon and Ionic Liquid. Towards All Solid Devices.

Khryslyn ARAÑO[a], Dominique GUYOMARD[a], Maria FORSYTH[b], Nicolas DUPRÉ[a], Bernard LESTRIEZ[a], Jean LE BIDEAU[a], Patrick HOWLETT[b], Robert KERR[b]

[a] *Institut des Matériaux Jean Rouxel, UMR 6502 CNRS, 2 rue de le Houssiniere, 44300 Nantes, France*
[b] *Instiute for Frontier Materials, Deakin University, Geelong, Victoria 3220, Australia*

Li-ion batteries (LiBs) are one of the most promising energy storage technologies owing to their high energy density and their long lifetime. Today, emerging applications such as electric vehicles and intelligent power grids require higher energy densities and retention of cycling capacities but also increased safety requirements. Among the negative electrode candidate materials, silicon is one of the most attractive alternatives to graphite due to its natural abundance and very high gravimetric capacity (3579 vs. 372 $mAhg^{-1}$ against graphite). In commercial LiBs, electrolytes based on carbonates are used and have been identified to suffer from degradation during charge-discharge cycles, leading to the uncontrolled evolution of the solid electrolyte interphase (SEI). Ionic liquid electrolytes are an appealing alternative to carbonates because of their stability, enabling control of the SEI. Moreover, all-solid batteries are a solution envisaged to obtain an increased security. In the project, two innovative and promising ways will be studied in order to meet the said objectives: 1) Optimization of the electrolyte composition based on ionic liquid electrolytes by understanding the formation and the evolution of the SEI on the silicon electrode, and 2) development of an ionogel that will serve both as the electrolyte and the separator, by the confinement of the ionic liquid in a porous silica matrix.

Previous results on Si anode studied in half-cell configuration, i.e. vs. Li foil, have shown that ionic liquid electrolytes (e.g. P_{1114}FSI with 3.2 M LiFSI) have higher capacity and better cyclability compared to conventional carbonate-based electrolytes such as LP 30 and LP 30 with FEC[1]. These findings will serve as a benchmark and the project will ultimately investigate a family of ionic liquids based on phosphonium and pyrrolidium cations and FSI and TFSI anions.

Keywords
Lithium ion battery, silicon anode, passivation layer, ionic liquid electrolytes, solid electrolytes, ionogels

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Poster

Effect of small organic molecules on the adsorption and transport of radionuclides in clay materials : From Molecular Modeling To Environmental Fate !

Debashish BANERJEE [a], Andrey KALINICHEV [a]

[a] *Laboratoire Subatech – (UMR 6457) IMT Atlantique, 4 rue Alfred Kastler, 44307 Nantes cedex 03, France*

Safe and sustainable nuclear waste disposal poses major scientific challenges to the efforts to minimize the environmental footprint of nuclear energy for extremely long periods[1,2]. It has become an international consensus that geological disposal is the most appropriate way for the confinement and disposal of long lived high level nuclear waste. The geological disposal is based on a multi-barrier concept where clay minerals are considered in engineered and geological barriers.

Cesium-137 (^{137}Cs), an important fission product from the irradiation of uranium based fuels and it has been released in the past to soils and waters as a result of nuclear accidents or weapon testing. Radio-cesium always exists as the monovalent cation Cs^+, which has very high solubility and mobility, thus being a very relevant element from environmental point of view. Cesium migration is mostly controlled by sorption onto mineral surfaces; it is mainly adsorbed onto clays by ionic exchange [3]. Many solids have been under study for Cs retention [4] but the barriers comprised of clay materials are reported to be the most effective for its retardation. The Callovo-Oxfordian[5] clay rock formation (Meuse/Haute-Marne, France) commonly known as COx is the potential host rock for long term nuclear waste repository in France. The clayey component of COx consists mainly of illite, smectite and interstratified illite/smectite (I/S) clay minerals. It constitutes a natural external barrier for limiting these hazardous radionuclides by its CEC (cation exchange capacity) to uptake these contaminants by adsorbing them thereby restricting their transfer towards biosphere[6]. On the contrary, organic molecules that are released from nuclear waste packaging containers along with the subsequent degradation products, severely challenge our principal host rock's capacity by altering radionuclides uptake, transport in geological barrier etc. These organic complexing species are therefore not only known to affect radionuclide mobility in the environment but also affects the cementitious materials used in underground vault construction [7, 8, 9].

In our work, we propose to perform atomistic computer simulations of a simplified but realistic model ternary system [radionuclides (RN's), organic molecules (OM), COx (sedimentary clay rich host rock)] and quantitatively analyze these effects in order to increase the fundamental understanding of the various physical and chemical mechanisms controlling the interactions between them.

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Poster

Multifunctional ligands based on TTF-Triphenylamine-Terpyridine: synthesis and complexation studies

Yohan CHERET, Abdelkrim EL-GHAYOURY

University of Angers, Laboratoire MOLTECH-Anjou, UMR 6200, 2 Boulevard Lavoisier 49045 Angers (France)

We report the synthesis, characterization and physicochemical properties of multifunctional ligands and their corresponding metal complexes (Figure 1). These ligands are based on Terpy-TPA-TTF, an electron donating Triphenylamine (TPA) core bearing a tetrathiafulvalene as an electron-rich and redox active unit and the Terpyridine (Terpy) as the chelating fragment. These ligands are prepared in order to synthesize transition metal complexes with original structural and electronic properties and to study the influence of the metal cations on these properties. A focus will be made on the possibility to build electroactive metallosupramolecular architectures.[1] Complexes will be also used as active materials for NonLinear Optical (NLO) applications as it has been previously shown in our laboratory with other TTF based multifunctional ligands.[2, 3] And finally complexes will be used as potential precursors for the preparation of radical cation salts by the use of electrocristallisation technique and therefore to obtain (semi)conducting crystalline materials.

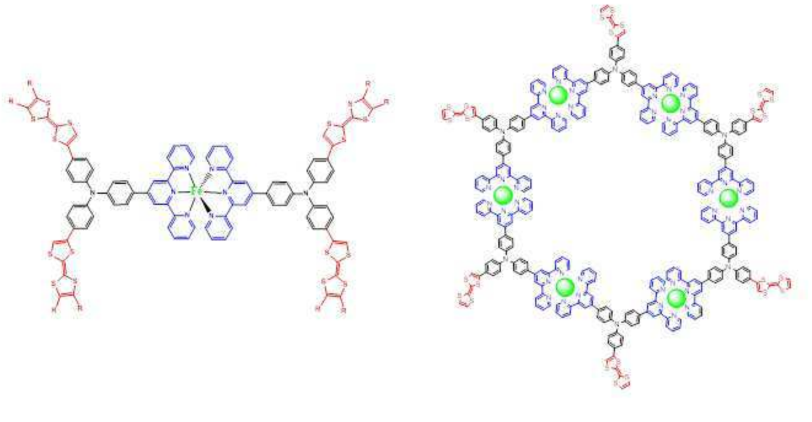

Figure 1 : Target mononuclear complex (left) and hexagonal metallomacrocycle (right)

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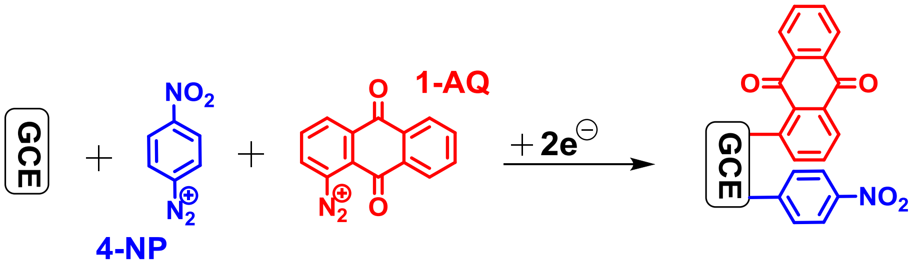
Poster

Elaboration of electro-actives surfaces by diazonium salts reduction

Ismael COULIBALY[a], Tony BRETON[a], Christelle GAUTIER[a], Eric LEVILLAIN[a]

[a] *Laboratoire Moltech-Anjou, UMR 6200 CNRS, Université d'Angers, 2 boulevard Lavoisier, 49045 Angers Cedex (France)*

The goal in this work is to study the reactivity of electrogenerated layers on Glassy Carbon Electrode (GCE) by diazonium reduction. Several investigations have been achieved across literature to understand the physico-chemical properties of these molecules in order to develop new functional materials. In our case, we are focused on mixed layers involving 4-Nitrobenzenediazonium[1] (4-NP) and 1-Anthraquinonediazonium[2] (1-AQ). These molecules have been simultaneously grafted onto GCE by electrochemical reduction as described below:



After grafting, the mixed layers were characterized by exploiting their electroactivity. We have shown that a fine modulation of the surface coverage of each entity can be obtained by varying the diazonium salt concentration ratio. This approach could be extended to the preparation of bi-or multifunctionalized surfaces, namely applied to biosensors,[3] electrochemical capacitors[4] or nanoelectronics.[5]

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Poster

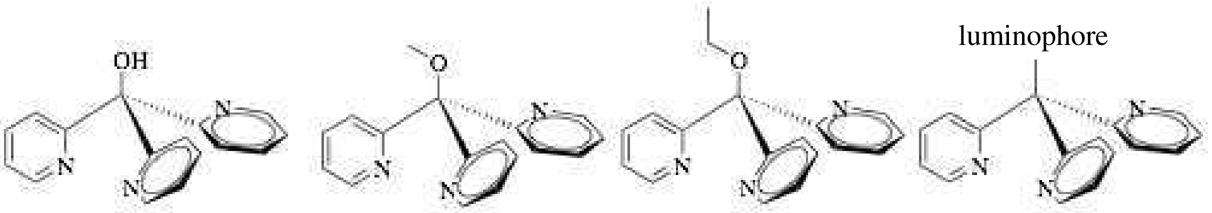
polyfunctional materials based on tris-(pyridyl)methane ligands

Emmelyne CUZA[a], Françoise CONAN[a], Smail TRIKI[a]

[a] *CNRS 6521, CEMCA (Laboratoire de Chimie Electrochimie Moléculaires et Chimie Analytique), Faculté des Sciences et Techniques -6 avenue Victor Le Gorgeu, F-29200 Brest France*

e-mail : Emmelyne.Cuza@univ-brest.fr

The design of new coordination complexes exhibiting the spin crossover phenomenon (SCO) is one of the most relevant and challenging questions in the field of magnetic molecular materials. In such systems, the magnetic state can be switched from the high-spin (*HS*) to the low-spin (*LS*) configuration through external stimuli such as temperature, pressure, magnetic field or light irradiation. The SCO phenomenon occurs in the d^4-d^7 transition metal complexes, but the most studied examples to date are those based on Fe(II) (d^6 configuration), for which a paramagnetic-diamagnetic transition from the *HS* ($S = 2$, $^5T_{2g}$) to the *LS* ($S = 0$, $^1A_{1g}$) state is observed. We and others have recently reported a very scarcely investigated approach consisting on the use of functionalized tris-(pyridyl)methane ligands (tpcR) ligands (Scheme 1) to design new SCO anionic mononuclear or neutral polynuclear systems. In addition, the chemical flexibility of such ligands can be viewed as an excellent starting point for the preparation of new parent polypyridyl ligands, involving luminophore groups, appropriate for the design of new functional materials exhibiting SCO and photoluminescent behaviours. In this context, we decided to study various simple substitutions (R = OH, -OMe, -OEt …) before substituting with a more sophisticated groups such as luminophore one's.



Scheme 1. Examples of prepared functionalized tris-(pyridyl)methane ligands (tpcR) ligands

We report herein the synthesis, the thermal variation of the crystallographic structural data and magnetic properties of new series of SCO Fe(II) complexes based on tpcR (OH, -OMe, -OEt …) ligands.

Poster

Integration of the ALICE muon spectrometer geometry in the O^2 software

Florian DAMAS[a,b]

[a] *Laboratoire Subatech, UMR 6457 CNRS, IMT Atlantique, 4 rue Alfred Kastler, Nantes*
[b] *Institut de recherche sur les lois fondamentales de l'Univers, CEA Saclay, rue de l'orme des merisiers, Gif-sur-Yvette*

A Large Ion Collider Experiment (ALICE) is one of the experiments of the LHC, the world's largest accelerator, at CERN. Its detector has been designed to study the properties of nuclear matter in the extreme conditions reached in ultra-relativistic heavy-ion collisions. At the end of 2018, the LHC will be stopped for 2 years during which its experiments will undergo more or less important upgrades. The ALICE collaboration wishes to benefit from the optimal potential of the LHC to collect as much data as possible.

The planned data rate (1 TB/s for Pb-Pb collisions) requires to completely revise the ALICE Computing Model. The O^2 project aims to reduce the data volume read out from the detector as much and as early as possible during the data-flow and before its storage. This new software will have for main role to perform the detector calibration and data reconstruction at the same time as the data acquisition.

The current ALICE simulation software does not allow to achieve these goals and some parts must be modified for their integration in O^2. In this context, a new way to model the geometry of the muon spectrometer has been developed. In particular, porting this geometry to O^2 gives the opportunity to make changes that could improve the simulation, and thus the future physics results.

Communication Poster

Study of the scale-up electrochemical reactor with a fixed bed three-dimensional cathode for the degradation by electro-Fenton with the Fe-EDDS complex of persistent pollutants in the water

Lionel DOMERGUE[a], Nicolas CIMETIÈRE[a], Sylvain GIRAUDET[a], Didier HAUCHARD[a]

[a] *Institut Sciences Chimiques de Rennes, UMR CNRS 6226, École Nationale Supérieure de Chimie de Rennes, 11 allée de Beaulieu, CS 50837, 35708 Rennes*

Advanced Oxidation Processes (AOP's) are commonly used for the removal of refractory pollutants during water treatment. Electro-Fenton process is promising technologies since the production of $HO^\bullet$ precursors (Fe^{2+}/H_2O_2) are in-situ formed in acidic medium (pH 3). Electro-Fenton only requires the use of catalyst (ferric or ferrous ions) in small amount [1]. Catalyst as well as the hydrogen peroxide is (re)generated according the following equations:

$$2O_2 + 2H_3O^+ + 2e^- \rightarrow 3H_2O_2 \text{ (E}^\circ = 0.69\, V_{/ENH}) \qquad \text{(Equation 1)}$$

$$\mathrm{H}_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^\cdot \quad \text{(Fenton's reaction)} \qquad \text{(Equation 2)}$$

$$\mathrm{Fe}^{3+} + e^- \rightarrow \mathrm{Fe}^{2+} \ (E^\circ = 0.77_{/ENH}) \qquad \text{(Equation 3)}$$

Moreover, electro-Fenton process has demonstrated a potential capacity of treating persistent chemical pollutants [1]. This process is very interesting but requires working in an acid medium (pH = 3). One major drawback of these treatments is the need for a low pH as iron precipitates at higher pH [2]. Moreover it can be a brake to be developed in the industrial environment for the treatment of water. In recent published works, the use of a new complexing agent of iron, ethylenediamine-N,N′-disuccinic acid (EDDS) as a safe and environmentally being, was investigated for environmental remediation purposes [3]. The addition of EDDS was used to extend the useful range of the Fe(III)/H_2O_2 system to neutral pH conditions preventing iron precipitation and so producing more oxidizing species [4]. The Fe(III)−EDDS 1:1 complex is stable in aqueous solution under neutral pH conditions and photochemically efficient [5] but not investigated in electro-Fenton conditions. In this work, our goal is to work on the use of the Fe-EDDS complex in an electro-Fenton process. It will be studying the performances of the method compared to classical electro-Fenton and to evaluate the limits of this process. The work will be to develop the process with complex Fe−EDDS in electro-Fenton to degrade a molecule soluble Bisphenol A (300 mg.L^{-1} at pH=3) and less soluble sodium Diclofenac (2.36 mg.L^{-1} at pH=3) at neutral pH (5,6,7). Electrochemical reactor was a plug-flow with a fixed bed three-dimensional cathode consituted by glassy carbon pellets. Results have been obtained on a little volumetric reactor (1.5 L) and on a great volumetric reactor (15L).

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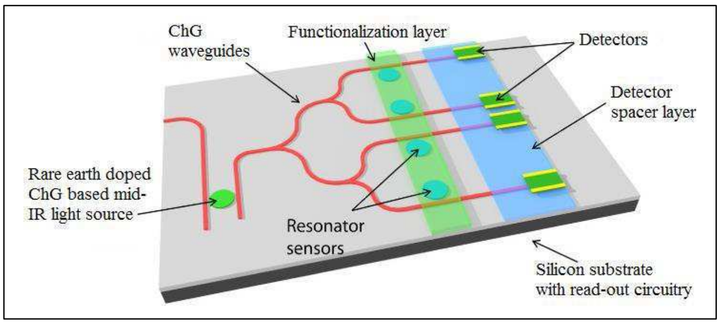
Poster

Rare earth doped chalcogenide mid-infrared luminescent integrated waveguides for chemical sensing

Walid EL AYED[a], Loïc BODIOU[a], Jonathan LEMAITRE[a], Isabelle HARDY[b], Emeline BAUDET[c], Virginie NAZABAL[c], Joël CHARRIER[a]

[a] Université de Rennes, CNRS, Institut Foton - UMR 6082, F-22305 Lannion, France
[b] IMT Atlantique, CNRS, Institut Foton - UMR 6082, F-29238 Brest, France
[c] Université de Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France

Integrated ridge waveguides based on Praseodymium ions (Pr^{3+}) doped selenide glasses $Ga_5Ge_{20}Sb_{10}Se_{65}$ have been fabricated by RF magnetron sputtering followed by UV photolithography and dry ICP-RIE etching[1]. Using light pumping at a wavelength of 1550 nm, mid infrared (mid-IR) photoluminescence (PL) was detected at room temperature within a spectral range from 2.5 to 5.5 µm, which overlaps with strong absorption bands of various atmospheric pollutants (CO, CO_2, NO_x, CH_4…) .
Mid-IR light sources are today among the most studied photonic devices as they can be used in many applications ranging from molecular spectroscopy, medical diagnostics, thermal imaging, environmental remote sensing to military armament. However, most current mid-IR photonic devices are bulky and/or costly which challenges the affordability and practical use of such devices on remote locations. Thus, a solution is to develop new materials and related appropriate micro-processing technologies in order to achieve compact, cost effective and reliable mid-IR photonic devices. Chalcogenide glasses[3] (ChG) display low phonon energies (~150-400 cm^{-1}), high and tunable refractive indices (~2-3.5), and good chemical stability. They can also be deposited as thin films and doped with mid-IR luminescent ions such as Pr^{3+}, Dy^{3+} or Tb^{3+}. They are therefore a promising alternative to efficiently emit and guide mid-IR radiations (2.5-20µm). This poster will highlight the importance of mid-IR spectral range for environmental applications. The processing and mid-IR optical characterization of rare earth doped chalcogenide integrated photonic structures will be described. Finally the relevance of these devices for environmental sensing will be presented.



Figure[2]: schematic illustration of the considered photonic integrated circuits based chemical sensor.

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Communication orale ☐ Poster [X]

Investigation of a wetland contaminated by uranium mine tailings in Central France

Andreas Fichtner [a,b], S. Sachs [b], G. Montavon [a], T. Stumpf [b]

[a] *Laboratoire Subatech, UMR 6457, IN2P3/CNRS/IMT Atlantique/Université de Nantes, 4 rue Alfred Kastler, BP20722, 44307 Nantes Cedex 3, France*

[b] *Institute of Ressource Ecology, Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstr. 400, 01328 Dresden, Germany*

The release of uranium from mine tailings may present a hazard to the environment, which is the reason for the monitoring of the relevant storage sites in many countries. Studying the behavior of released radionuclides at these sites serves to better estimate the local risk and can help to improve the understanding of the geochemistry of the involved contaminants, e.g. for the application in transport modelling.

The storage site Roffin, located in the Region of Auvergne, France, contains approximately 30 000 t of mill tailings from the adjacent processing plant of the same name, which operated from 1947 to 1956. After the shutdown of the plant, the responsible operator has remodeled the site several times over the decades, in order to meet updated environmental standards [1].

Recent gamma-ray surveys have shown elevated radiation levels alongside a creek downstream of the storage site, especially in a wetland area in some two hundred meters distance of the site. Drill cores taken in this area show uranium concentrations up to 2000 ppm in the upper 30 cm, with peak concentrations in a whitish, clayey layer with a thickness of about 5 cm at a depth of 20 cm. Besides this anomalous layer, the soil is of the histosol type, with very high contents of organic matter and mostly saturated with water. The goal of our study is to identify the involved uranium species in the solid and aqueous phases, in order to understand the influence of discharge history and geochemistry on the risk presented by this contamination.

Sequential extractions performed on the different layers of the soil indicate a majority of the uranium to be bound to soil organic matter. Yet scanning electron microscopy analysis (SEM) of the white layer shows the presence of particles containing high uranium concentrations with sizes around 10 µm. Energy dispersive X-ray spectra (EDS) of some of these particles give compositions corresponding to a specific mineral processed in the plant, which is Parsonsite [Pb2(UO2)(PO4)2]. Dating the soil with the C-14 of the soil organic matter and the depth profile of Cs-137 from nuclear fallout further suggests that the origin of the white layer is connected to the active period of the plant. X-ray absorption spectroscopy performed on the soil shows a variable distribution of U(IV) and U(VI) in the different layers.

Further studies aim to quantify the distribution of uranium between the different solid phases of the soil, as well as the identification of the main species in the porewater.

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Poster

Study of charmonium probes in high multiplicity pp collisions with the ALICE detector. The ALICE Muon Forward Tracker for run 3 at LHC.

Manuel GUITTIERE[a] for the ALICE collaboration

[a] *SUBATECH, CNRS/IN2P3, Université de Nantes, IMT Atlantique, Nantes, France*

Manuel.Guittiere@subatech.in2p3.fr

Considering actual knowledge in the field of particule physics, the Standard Model predicts, through Quantum Chromodynamics (QCD), two distinct states of hadronic matter. At low energy density, quarks and gluons are confined within hadrons, constituting the ordinary matter. At very high energy density conditions (above ~ 1 $\mathrm{GeV/fm^3}$), a deconfined state of matter, the Quark-Gluon Plasma (QGP), is expected to be created. The characterization of QGP is the main aim of the ALICE (A Large Ion Collider Experiment) research program. The ALICE experiment is located at CERN Large Hadron Collider (LHC) where QGP is expected to be produced in ultra-relativistic heavy ion collisions. One of the major highlights of LHC results is the observation of QGP-like phenomena in high multiplicity pp and p-Pb collisions, where QGP is not expected to be formed. The properties of QGP are indirectly studied measuring observables called probes since their production and behavior can be affected by the medium. Charmonia probes such as J/Ψ and $\Psi(2S)$ are hadrons composed of a quark pair charm - anti-charm and formed at early stages of the collisions so they could interact with QGP. The production and properties of these probes are measured through their dimuon decay channel with the ALICE muon arm. One of the goals of my thesis, is to search for QGP-like phenomena in the production of charmonium in high multiplicity pp collisions at 13 TeV.

The Muon Forward Tracker (MFT) is an upgrade of the ALICE detector designed to allow exclusive measurements from run 3 (2020) at LHC. The MFT is a five station silicon MAPS detector allowing to determine, with high resolution, the vertex of the muon tracks. The MFT will allow to distinguish prompt and non-prompt charmonia to reduce the background below the charmonium resonances, hereafter to noticeably improve the measurements of charmonium by the ALICE detector. The second goal of my thesis is the construction, installation and simulation of the MFT detector.

In this poster I will present the first preliminary results for $\Psi(2S)$ to J/Ψ ratio in high multiplicity pp collisions and an overview of the experimental apparatus and particularly the MFT design and features.

Communication orale ☐ **Poster** ■

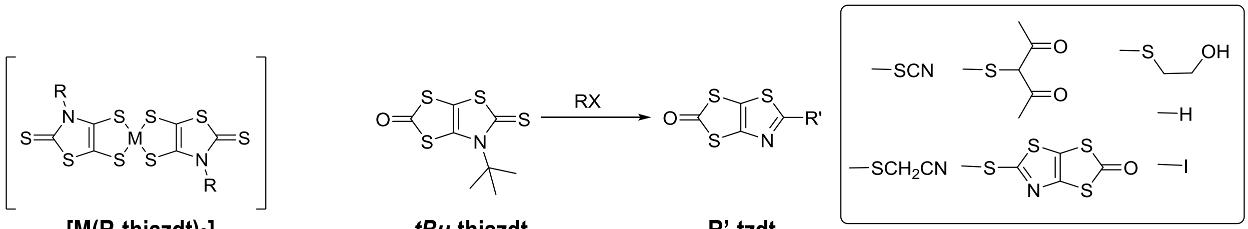
Towards highly conducting metal bis-dithiolene complexes

Hadi HACHEM,[a] Olivier JEANNIN,[a] Marc FOURMIGUE,[a] and Dominique LORCY[a]

[a] *Univ Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France*

Metal bis-(dithiolene) complexes have been thoroughly studied as precursors of molecular conductors.[1-2] Among the numerous types of dithiolene ligands, (N-alkyl-1,3-thiazoline-2-thione-4,5-dithiolate) ones (abbreviated R-thiazdt), have been the subject of increasing interest due to their electron rich character, coupled with the ease to functionalize the thiazole moiety with various groups (N-R).[3] This allows the modulation of the redox, as well as the structural properties of the complex, and therefore the electronic properties of its corresponding material. That modulation however, is limited by the available R groups of primary amines which are the starting materials.

Recently our team demonstrated an unprecedented transformation of N-tert-butyl-1,3-thiazoline-2-thione heterocycles (*tBu*-thiazdt) into 2-alkylthiothiazole derivatives (RS-tzdt) in the presence of electrophiles (R-I, R= Me, Et).[4] This reactivity opens the way to a novel series of dithiolene ligands, and the capability of introducing functionality that was unattainable with the conventional synthetic route to the thiazdt ligands. Herein we report the synthesis and the structural properties of seven novel R-tzdt functional ligands (R= iodide, hydrogen, acetyl acetone, acetonitrile, thiocyanate, ethyl alcohol, and a dimer), and two of their corresponding gold dithiolene complexes.



[M(R-thiazdt)₂] *tBu*-thiazdt **R'-tzdt** **R'**

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Poster

Synthesis and electrochemical study of mixed-valence triiron clusters derived from dinuclear models of the active site of [Fe-Fe] hydrogenases

Ahmad HOBBALLAH[a], Catherine ELLEOUET[a] , François PETILLON[a], Philippe SCHOLLHAMMER[a]

a CNRS, CEMCA (Laboratoire de Chimie Electrochimie Moléculaires et Chimie Analytique), Faculté des Sciences et Techniques -
6 Avenue Victor le Gorgeu, CS 93837, 29238 Brest, France cedex

The structural determination of [Fe-Fe]-hydrogenases has led during the two last decades to the reinvestigation and a huge development of iron carbonyl thiolate complexes chemistry.[1] The use of well-known organometallic tools has allowed to reproduce some chemical and structural precedents of the natural site which have contributed to a better understanding of the chemistry of the H-cluster.[1] During these studies, very original side products featuring quasi linear tri- and tetranuclear arrangements have been synthesized.[2] These novel polynuclear complexes do not model directly the H-cluster of the [Fe-Fe]-hydrogenases but their chemistry is related.

Some years ago, the unexpected formation of the trinuclear, mixed valence {Fe(I)Fe(II)Fe(I)} species, $[Fe_3(CO)_5(P^{Ph}{}_2N^{Ph}{}_2)(\mu\text{-pdt})_2]$ ($P^{Ph}{}_2N^{Ph}{}_2 = (PPhCH_2NPhCH_2)_2$; pdt = propanedithiolate) was reported as a side product, from the reaction between $[Fe_2(CO)_6(\mu\text{-pdt})]$ with $P^{Ph}{}_2N^{Ph}{}_2$ through a non-established mechanism.[3] The reminiscence of the original structure of this compound with mixed valent Fe(I)Fe(II) systems and the possible efficient activity, as electrocatalyst towards H^+/H_2 conversion, of such trinuclear compounds led to define a general route to elaborate this class of derivatives which can be considered formally as constituted by the combination of a diiron framework and a mono iron moiety as a metalloligand.[4]

This communication will present the extension of this strategy for the preparation of a series of novel triiron complexes $[Fe_3(CO)_5(\kappa^2\text{-dppe})(\mu\text{-dithiolate})(\mu\text{-pdt})]$ with different dithiolate bridges in order to tune their electronic and steric properties. Their spectroscopic characterizations and their electrochemical properties will be presented.

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Poster

Embedded optical system for turbofan engine exhaust gas sensing

Xavier INSOU[a,b], Monique THUAL[a], Loïc BODIOU[a], Sébastien CLAUDOT[b]

[a] *Univ Rennes, CNRS, Institut Foton – UMR 6082, F-22305 Lannion, France*
[b] *Souriau Esterline Connection Technologies, RD323, Champagné*

There is a growing need for compact, fast and cost-effective sensors able to detect small traces of environmental pollutants and toxic vapors in a variety of atmospheric, security, healthcare, agri-food and industrial applications. Mid-infrared (mid-IR) spectroscopy is nowadays considered as a routine analysis and sensing tool providing highly discriminatory information on organic and inorganic molecules due to the excitation of vibrational and rotational transitions that are specific to these species.

In particular, European aeronautic research program CleanSky2 strongly requests to detect critical molecules like CO_2, NO_X and H_2O, as well as other organic compounds and fire extinction agents[1].

This PhD project aims at implementing a novel measurement system based on mid-IR absorption for in-flight monitoring of gaseous pollutant emissions, as presented in Fig. 1. The proposed system will need to comply with aircraft environments, especially in terms of operating temperature, pressure, vibration and corrosion. In addition, self-cleaning, auto-calibration ability, and modular design is expected to ensure reliability and durability.

The system design will require simulations of the mid-IR light/gas interaction and species cross sensitivity, as well as the development of a functional mock-up to perform preliminary sensing experiments in relevant conditions.

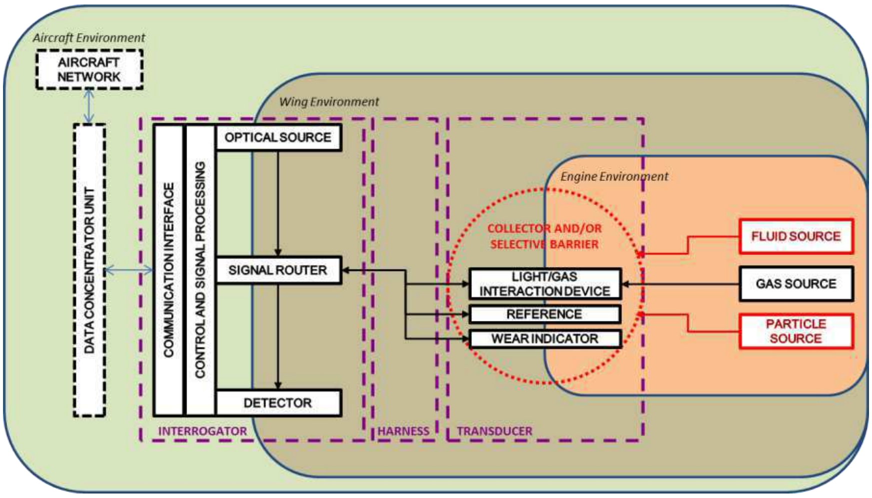

Figure 1 – Global diagram of an aircraft engine exhaust gas measurement system

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Poster

Generation of high energy microsecond pulses from a hybrid regime of oscillation in a fiber laser

Meriem Kemel[a], Fatma Ben Braham[a], Andrey Komarov[b], Georges Semaan[a]
Mohamed Salhi[a], And François Sanchez[a]

[a] *Laboratoire de Photonique d'Angers, E.A 4464, Université d'Angers, 2Bd Lavoisier, 49045, Angers cedex 01, France*
[b]*Institute of Automation and Electrometry, Russian Academy of Sciences, Acad. Koptyug, Pr. 1, 630090 Novosibirsk, Russia*

meriem.kemel@univ-angers.fr

Phase-locked fiber lasers are promising generators of light pulses used in both scientific research and technological applications such as spectroscopy, biomedical, metrology, etc. The mode-locking in fiber lasers enables to obtain several types of pulses such as solitons, dissipative solitons, similaritons, etc. This pulses are organized with different distributions (harmonics, bound states ...).

Because of the energy quantification in anomalous dispersive laser configurations, the rise in energy pulses is difficult. As the pump power increases, the pulses undergo a wave-breaking which leads to the generation of multiple pulses and then the limitation of pulse's energy.
To circumvent this problem, new techniques concerning the optimization of the laser cavity length are investigated, leading to the generation of pulses like Dissipative Soliton Resonance or noise-like which experience an energy increase by increasing the pump power.

In a recent publication[1] Komarov et al. propose, by the mean of computer simulation, a new cavity configuration for the generation of energetic and giant pulses by inducing an optical delay in the fiber cavity without wave-breaking. This configuration is investigated experimantally by our group.

To conclude, we confirm experimentally the simulation results. We get pulses which don't undergo wave-breaking, with durations ranging from 3 to 5 μs and energies between 0.5 and 5 μJ

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Poster

Eco-friendly and fast synthesis of polypyrrole and reduced graphene oxide foam nanocomposite and its application to supercapacitors

Samir KRIDI[a], Dominique DEBARNOT[b], Fabienne PONCIN-EPAILLARD[c], Nacerddine HADDAOUI[d]

[a,b,c] *Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, Le Mans*
[d] *Université Ferhat ABBAS Sétif-1, Algérie*

The research on graphene has become one of the most attractive scientific topics at present, because this new carbon material possesses unique physicochemical properties which impart it with great potentials in various application areas [1,2]. In this work, we report a fast and environmentally friendly method to synthesize plasma-polymerized pyrrole (ppPY) and reduced graphene oxide foam (rGO) nanocomposites using plasma-enhanced chemical vapor deposition (PECVD). The rGO foam was synthesized by plasma assisted simultaneously exfoliation and reduction of graphene oxide foam (GO) which was prepared by freeze drying of aqueous GO suspensions. Then nano-size ppPy particles are homogeneously decorated by pulsed plasma polymerization onto individual rGO sheets to form nanostructured composites (rGO-ppPY). The different materials were characterized by RAMAN, FTIR, AFM, MEB, MET, cyclic voltammetry, and UV-VIS spectroscopy. The influence of power, pulse time, duty cycle and time deposition on the morphology and the chemistry of the resulting plasma polymerized pyrrole layers was evaluated. It was shown that the use of a pulsed plasma as a means to minimize fragmentation is most efficient under very low power inputs. Homogeneous ppPY films having a thickness of 2 nm were obtained.

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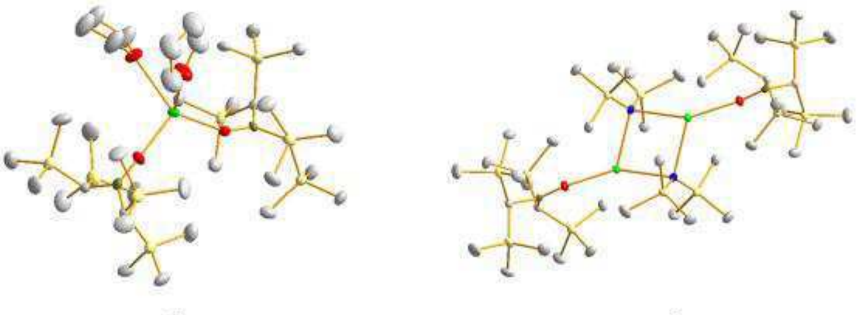
Poster

SYNTHESIS OF THE FIRST BARIUM BOROXIDE COMPLEXES AND APPLICATION IN DEHYDROCOUPLING

Erwann LE COZ [a], Yann SARAZIN*, Jean-François CARPENTIER [a]

[a] *Institut des Sciences Chimique de Rennes, Université Rennes 1, UMR CNRS 6226, Campus de Beaulieu, 35042 Rennes France*

Alkoxide ligands, $[RO]^-$ remain one of the most used ligand in inorganic and coordination chemistry since fifty years. In heavy alkaline earth metals chemistry (Ca, Sr and Ba) the synthesis of alkoxide complexes is a problem because of the high electron density located on the O atom which result in a tendency to bridge between two or more different metal centers. This bridging ability cause the formation of multinuclear or polymeric compounds. This is why alkaline earth alkoxides are poorly soluble and complicated to use and also this make the preparation of heteroleptic compounds really difficult.
Here we report the synthesis of different highly soluble homo and heteroleptic boroxide complexes with boroxide ligand as electron deficient alkoxides[1]. Boroxides are alkoxides with a boron atom directly connected to the oxygen in order to decrease the electron density of the oxygen and so decrease the bridging tendency of these ligands.



1 2

Figure 1 Structure of $\{Ba[OB(CH(SiMe_3)_2)_2]_2.THF_2\}$ **1** and $\{Ba[OB(CH(SiMe_3)_2)_2][N(SiMe_3)_2]\}_2$ **2.**

An application for boroxide complexes is the catalytic formation of borasiloxanes by dehydrocoupling between borinic acids and silanes.

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~~Communication orale~~ / Poster

Synthesis of amphiphilic copolymers applied to the crystallization of calcium carbonate particles in supercritical CO_2 by a continuous and eco-friendly emulsification process

Pierre LEGOUT[a,b], Olivier COLOMBANI[a], Guillaume LEFEVBRE[B], Marie BONNIN[b], Domitille LEFEBVRE[a,b], Brice CALVIGNAC[b]

[a] *Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, Le Mans, France*

[b] *Laboratoire Mint, Université d'Angers, INSERM-UMR 1066 et CNRS UMR6021, 4 rue Larrey CHU, 49933 Angers, France*

There are two technologies for the production of calcium carbonate by crushing and by precipitation (PCC).[1]

My project (SPEED, Pays de Loire) proposes a new strategy for developing PCC particles with controlled characteristics (polymorphism, size and structure) by a continuous and eco-friendly process. This continuous process is based on the formulation of a water / CO_2 supercritical emulsion (CO2sc) whose stabilization by amphiphilic diblock copolymer. In the literature, different copolymers have been used to stabilize water / CO_2sc[2] emulsions. Fluorinated surfactants are very efficient[3,] but they are toxic. In contrast, Pluronics® (copolymers based on polyethylene oxide (POE) and propylene oxide (POP))[4] are low in toxicity, but they are less effective. In addition, PDMS-b-PHEMA and PDMS-b-POE block copolymers also have a substitution interest which is reinforced by the strong CO_2philic character of the PDMS block. The objectives of my project consists (i) to synthesize copolymers with a PDMS block and (ii) to compare their water / CO2 interfacial activity with these (iii) commercial copolymers (Pluronincs®) in order to control the emulsion and the stabilization of aqueous droplets.

This poster will focus on the radical polymerization by reversible deactivation of active centers (PRDR)[5,6] of diblock copolymers PDMS-b-PHEMA as well as the characterization of water / CO_2 emulsions formulated with these polymers.

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Poster

Physical chemistry of confined ionic liquids

Angélique MARIE[a], Jean LE BIDEAU[a]

[a] *Institut des Matériaux Jean Rouxel (IMN), UMR 6502, Université de Nantes,2 rue de la Houssinière, 44322 Nantes cedex 3*

Ionic liquids are salts whose melting temperature is below 100°C at atmospheric pressure. At room temperature, they are liquids completely composed of ions. They have the characteristics of low flammability, very low vapor pressure and high thermal stability, and have also a large window of electrochemical stability[1]. They can be used as alternatives to organic solvents and are studied to replace (totally or partially) the organic electrolytes currently used in energy storage devices[2].
The use of ionic liquids in commercial electrochemical systems could be facilitated by integrating them into solid devices able to maintain their liquid properties, such as ionogels[3]. An ionogel is a hybrid solid structure consisting mainly of a liquid phase, the ionic liquid, which is confined in a solid porous matrix (organic or inorganic). Under the right conditions, the ionic conduction properties of an ionogel are close to those of the unconfined ionic liquid, or even improved[4]. It has also been observed that the confinement of an ionic liquid can lower its melting temperature, which makes it possible to maintain good ionic conduction properties even at low temperatures[5].

The aim of the thesis is to understand the effects of confinement on the physico-chemistry of ionic liquids, specifically by the study of phenomena at the interface.
The structure of the confining network (organic, inorganic or hybrid type) must be controlled to study its impact on the confinement of ionic liquids (coll. A. Galarneau, Montpellier). We will focus more particularly on the pore size and the chemical nature of the species on their surface. The ionic liquids will be chosen according to their chemical properties (protic, aprotic, coll. A. Balducci, Jena, Germany) and their structure, in order to highlight the possible impact of a modification of the chemistry or the symmetry of the system.
Depending on the interface and objects observed (ions, chemical functions) different characterization techniques are envisaged. Raman spectroscopy, near-IR diffuse reflection and NMR, to study interactions at the host-matrix-liquid interface as well as complex impedance spectroscopy, PGSE NMR, and quasi-elastic neutron scattering to study transport of loads.

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Poster

Tritium speciation in environmental samples

Anne-Laure NIVESSE[a,b*], Olivier PÉRON[a], Nicolas BAGLAN[b], Gilles MONTAVON[a]

*[a] Laboratoire Subatech, Groupe Radiochimie, UMR 6457, IN2P3/CNRS/IMT Atlantique/Université de Nantes, 4 rue Alfred Kastler, BP20722, 44307 Nantes Cedex 3, France (*nivesse@subatech.in2p3.fr*
[b] CEA, DAM, DIF, F-91297 Arpajon, France

Tritium is the radioactive isotope of hydrogen and can integrate organics molecules of living organisms by water cycle and form the organically bound tritium fraction (OBT). [1] In 2017, the IRSN published a report on the update of knowledge on tritium, [2] taking up some of the questions that have been waiting to be answered since the publication of the Livre Blanc du Tritium by ASN in 2010. [3] Among these, those concerning the behavior, fate and speciation of this radionuclide in the environment are still relevant.

OBT is usually distinguished into two forms: a non-exchangeable fraction (NE-OBT) and an exchangeable fraction (E-OBT) with the near environment. [4] However, there is no consensus on their definition and several variations can be found in the literature data base.

NE-OBT analysis involves an isotopic exchange step to remove E-OBT from a sample. The present method, where the dehydrated sample is covered with aqueous water, has the disadvantage of causing the dissolution of a part of the organic compounds of the sample, which can lead to an analytical bias. [5] A new method has been developed to overcome this potential solubilization. It consists of a tritium marking line, with a controlled and stable ratio (T/H), which makes it possible to determine the exchangeable hydrogen fraction α and to calculate the value of the TOL-NE. [6]

The work of this thesis aims to improve the global understanding of tritium exchange mechanisms in environmental matrices and to validate the E-OBT and NE-OBT information determined on the tritium marking line.

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Poster

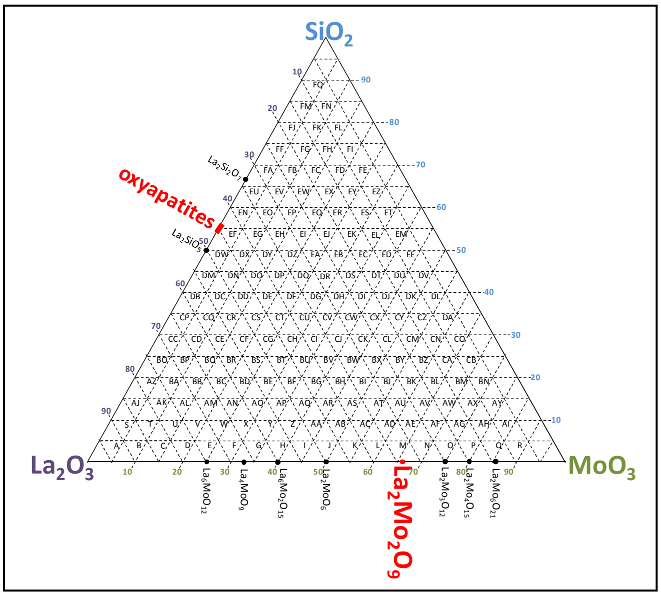
Exploration of the phase diagram $La_2O_3 – MoO_3 – SiO_2$

Antoine PAUTONNIER[a], Maud BARRE[a], Sandrine COSTE[a] and Philippe LACORRE[a]

[a] *Institut des Molécules et Matériaux du Mans, UMR CNRS 6283, Le Mans Université, Avenue Olivier Messiaen, Le Mans*

The Solid Oxide Fuel Cells allow to produce clean energy. These devices include an oxide-ion conductor as electrolyte material. Unfortunately, they are currently efficient only at high temperatures (~800°C). In order to improve their performance, their operating temperature has to be decreased by using electrolyte materials with high ionic conductivity properties at lower temperatures.

In this work, we explore the phase diagram $La_2O_3 – MoO_3 – SiO_2$ in order to find new phases with possible oxide-ion conductivity, by determining their structure and measuring their conduction properties. The diagram contains two already well known ionic conductors. On one hand, in 1995, Nakayama *et al.* **[1]** showed that the oxyapatite-type lanthanum silicate $La_{10}(SiO_4)_6O_3$ exhibits a ionic conductivity of $1.4x10^{-3}$ $S.cm^{-1}$ at 700°C. Nevertheless, that compound is difficult to shape (sintering temperature around 1700°C) and has a unidirectional conductivity. On the other hand, the studies realized by Lacorre *et al.* **[2]**, in 2000, evidenced that the compound $La_2Mo_2O_9$ presents a conductivity which can reach $6x10^{-2}$ $S.cm^{-1}$ at 800°C. However, the main drawback of this compound is its reducibility (in a reductive atmosphere, it becomes $La_7Mo_7O_{30}$ **[3]**).



The final aim of this work is, then, to find in this phase diagram compounds showing synergy of these properties while avoiding their problems.

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Functionalization of surfaces – Antifouling Coatings

Fanny PEIGNEGUY [a], Sylvie DABOS-SEIGNON [a], Magali ALLAIN[a],
Christine BRESSY[b], Charles COUGNON[a] and Frédéric GOHIER [a]

[a] Université d'Angers, CNRS UMR 6200, Laboratoire MOLTECH-Anjou, 2 bd Lavoisier, 49045 Angers cedex, France [b] Université de Toulon, Laboratoire MAtériaux Polymères-Interfaces-Environnement Marin (EA 4323 MAPIEM) CS 60584 -83041 Toulon cedex 9, France.

There are more than 4000 fouling organisms which colonize the surface immersed in the seawater such as bacteria, algae spores, barnacles, algae, mussels...The key steps of surface colonization are the formation of a conditioning film with adsorbed proteins or polysaccharides, then the bacteria come to fix reversibly before to create a matrix of exopolymers on which settle micro and macro organisms.[1] Consequently, the fouling is a great concern from the economic and environmental point of view for the naval industry. In the sixties, a new coating based on tributyltin was used as a biocide and proved to be very efficient. However, its toxicity for the non-targeted organisms leads to its ban in 2008 in France. So, other techniques are developed as paints based on copper or biocide. Functionalization of surfaces is also developed because it prevents from the adhesion or the degradation of the surface, notably immobilizing the poly(ethylene glycol) (PEG), enzymes, zwitterionic polymers or polysaccharides on the surface.[2] So, we would like to adopt the same strategy by grafting carbohydrates on surface. Indeed, carbohydrates have a neutral charge, a high hydrophilicity and are able to resist to the fouling.[3] In fact, carbohydrates act as a "water barrier" since a water layer takes place on the surface providing a repulsive force on the proteins. For this project, these carbohydrates would be also linked to electrostimulable linear conjugated system that would modify the surface polarity under oxidative potential. These systems would have the same role than the biocide but it would not be released in the seawater: it would be a BIO antifouling coating[1](Figure 1).

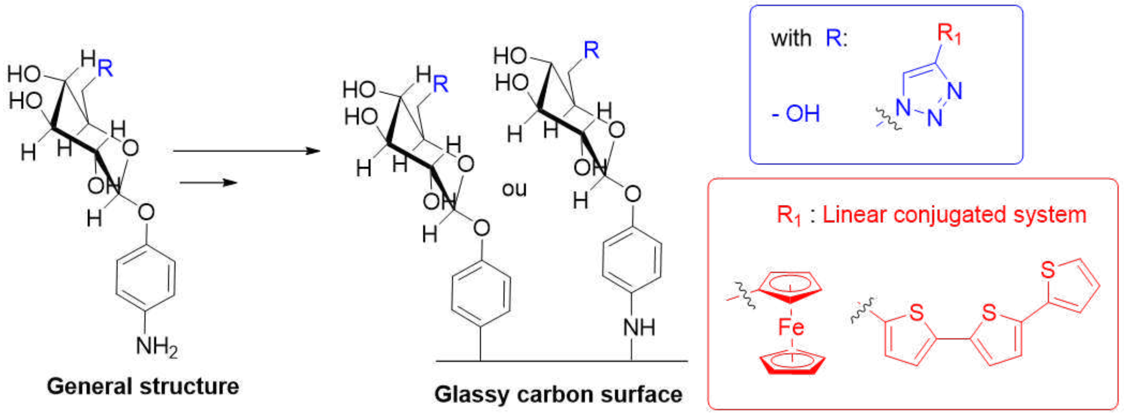

Figure 1 : Carbon Surface modification via aryldiazonium salt reduction[4] or amine oxidation

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[1] http://www.agence-nationale-recherche.fr/Projet-ANR-12-ASTR-0034

Poster

$CuGaSe_2$ growth optimization for tandem solar cell

Adrien RIVALLAND[a], Nicolas BARREAU[a], Ludovic ARZEL[a], Sébastien DUBOIS[b]

[a] *Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS-UMR 6502, 2 rue de la Houssinière, BP 32229, F-44322 Nantes Cedex 3, France*

[b] *Université Grenoble-Alpes CEA/LITEN, INES, 50 Avenue du Lac Léman, 73375 Le Bourget-du-Lac, France*

To surpass 30% conversion efficiency, tandem solar cells with crystalline silicon (c-Si) sub-cell seem to be one of the most promising architectures regarding the theoretical efficiency. Furthermore a monolithic two-terminal approach with wide bandgap thin films does not require a significant modification of the solar modules fabrication.

$CuIn_{1-x}Ga_xSe_2$ is a promising candidate thanks to its good efficiency around 22% for $x = 0.3$ (single junction). Nevertheless its bandgap is lower than the optimum value for a top-cell, which is around 1.7 eV. Such a value corresponds to $x = 1$. However the $CuGaSe_2$ record efficiency is too low ($\eta = 11.9\%$) for a tandem integration with c-Si. Hence, an optimization is needed to improve $CuGaSe_2$ co-evaporation process and adapt it for the substrates used on tandem applications.

We have chosen a **CuPRO** (**C**opper **P**oor / Copper **R**ich / Copper **O**ff) process to grow $CuGaSe_2$ absorbers on SLG/Molybdenum. During the process, the second stage allows the formation of large grains and the third reduces the defects concentration. In our work, we focus on the morphological and electrical impacts of the copper content during the first stage.

However, since the $CuGaSe_2$ growth depends on the nature of the substrate, further work is required in order to adapt the CuPRO process for silicon or oxides substrates, used for tandem solar cells.

Poster

3-Dimensional π-conjugated push-pull molecules for organic photovoltaics

Pablo SIMON MARQUES[a], José María ANDRES CASTAN[a], Martin BLAIS[a], Magali ALLAIN[a], Clément CABANETOS[a], Philippe BLANCHARD[a]

[a]*MOLTECH-Anjou, UMR CNRS 6200, University of Angers, 2 Boulevard Lavoisier, 49045 Angers, France*

pablo.simon@univ-angers.fr

In the framework of Organic Photovoltaics (OPV), the research has overwhelmingly focused on solution-processed conjugated polymer:fullerene blends.[1] More recently, small π-conjugated molecules have spread owing to their good photovoltaic performance as electron-donors[2] or electron-acceptors[3] combined with their good processability either in solution or by vacuum process. Regarding their chemical structure, 3-dimensional (3-D) molecules have received a particular attention due to their potential isotropic charge-transport properties, reduced crystallization and higher solubility than 2-D systems.

Tetracyanobutadiene (TCBD) moiety is an electron-withdrawing group (A) that has been used in π-conjugated push-pull molecules D-π-A for non-linear optics. This group confers a 3-D structure and a higher thermal stability to the push-pull molecule.[4] More recently, TCBD has been successfully used in organic solar cells by Leliège *et al.*[5] and since then many donor and acceptor materials for OPV including this functional group have been reported in the literature.

Here, we present the synthesis of a series of new unsymmetrical TCBD-based push-pull molecules exhibiting different aromatic scaffolds such as phenyl, naphthyl and pyrenyl moieties. Their electrochemical and optical properties will be described as well as the preliminary evaluation of their photovoltaic performance. The impact of the nature of the aromatic platform on electronic properties will be also discussed.

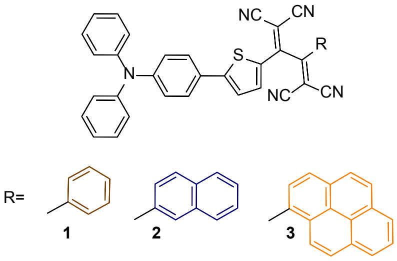

Figure 1. *Synthesized molecules.*

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Poster

BEAM ENERGY SCAN PROGRAM WITH EPOS MODEL

Maria STEFANIAK[a,b]

[a] *IMT Atlantique, 72 Rue Alfred Kastler, 44300 Nantes*

[b] *Warsaw University of Technology, plac Politechniki 1, 00-661 Warszawa, Polska*

Studies of collisions of highly accelerated ions are the key to understand the creation of quark matter. Experimental physicists put considerable effort in collecting information characterising the various processes occurring during such collisions. In order to describe such scenarios, complex models have been constructed, one of them being the EPOS approach. It applies Parton-based Gribov-Regge theory as an initial condition, introduces the core-corona approach, hydrodynamical evolution and hadronic cascades as well. The model is used by experimental physicist at the LHC or in cosmic ray physics.

At the Brookhaven National Laboratory, the STAR collaboration is currently investigating an interesting project called Beam Energy Scan. The QCD phase diagram is studied in order to understand the phase transitions close to the critical point, which should be in the energy domain studied in this program. Models have difficulties to describe this energy range properly. The aim of our investigation is to adapt the EPOS model to describe correctly collisions of ions with energies studied in the framework of the BES program.

The detailed description of the theory included in EPOS model will be presented. The energy dependence of the separation into the core and corona will be discussed, and the way it affects transverse momentum spectra of identified particles and the observables of the azimuthal anisotropy of expanding matter. The particles from the corona are strongly affected by the radial flow and the flow asymmetries. The results of different types of analysis of elliptic flow will be discussed. The simulation results for collisions of Au+Au at selected BES energies will be presented in comparison with the published STAR data.

Poster

PyDEF: an easy to use post-treatment software for ab-initio calculations

Adrien STOLIAROFF,[a] Emmanuel V. PEAN,[a] Camille LATOUCHE,[a] Stéphane JOBIC[a]

[a]Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France

Modern computational chemistry and physics have developed into a very helpful tool for the material scientist. The current landscape of scientific codes related to this discipline offers for the moment a tiny number of programs featuring a user-friendly interface. We have developed a post-treatment tool for VASP calculations called PyDEF[1] to balance this void. This program displays an ergonomic Graphical User Interface, which should allow both specialist and non-specialist scientists to use it. Publishable quality charts and all capabilities of the program are at the reach of a few clicks. Thanks to this software, one can plot Density of States (optionally with projections) and band diagrams, stability domains of materials, defect formation energies, optical indices (ε_1, ε_2, n, k, R), as well as compute effective masses of charge carriers, defect concentrations.

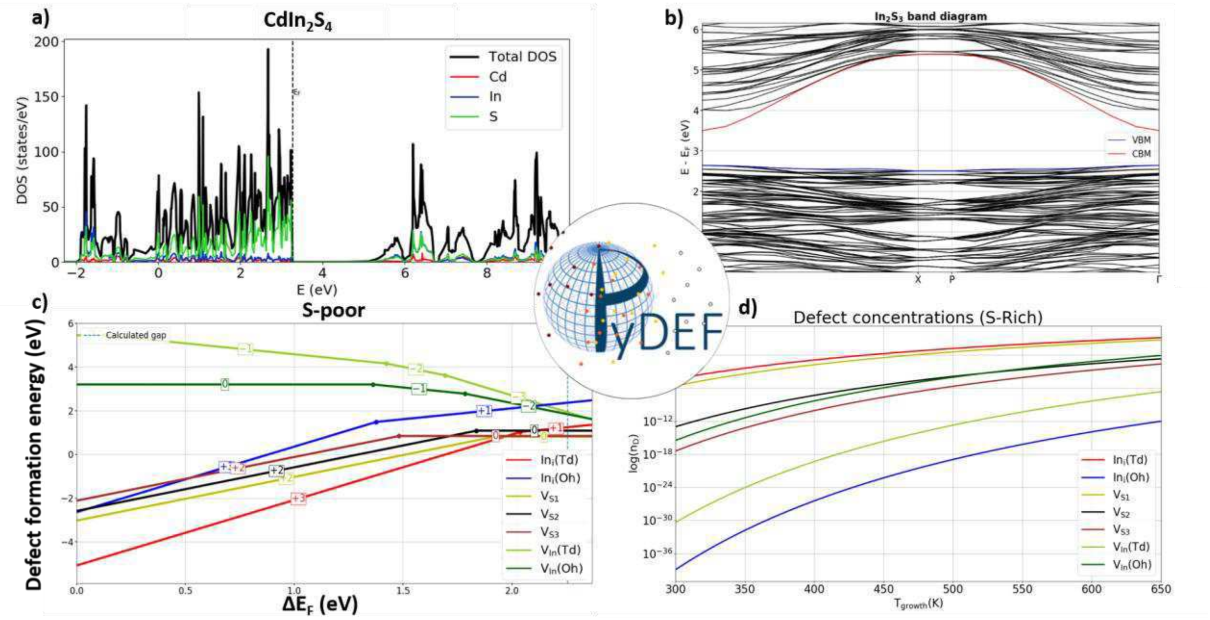

Figure: a) Density of States, b) Band Diagram, c) Defect Formation Energy, d) Defect Concentration Plots by PyDEF

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Realization and characterizations of conducting ceramics based on ZnO doped by TiO_2, Al_2O_3 and MgO

Qianying SUN[a,b], Guorong LI[a], Barre MAUD[b], Zhenyong MAN[a], Jens DITTMER[b], Abdelhadi KASSIBA[b]

[a] *Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*
[b] *Institut des Molécules et Matériaux du Mans, Le mans Université du Maine, 72085 LE MANS*

ZnO with wurtzite structure is a well-known semiconducting oxide (SCO), which has a wide set of applications in thermoelectric devices, varistors, gas sensors, transparent electrodes, solar cells, liquid crystal displays, piezoelectric and electro-optical devices. Intrinsically, ZnO is weakly n-type SCO due to native defects (Zn^i, V^o). However, the substitutional doping by metallic elements as (Al,Ti) give rise to a high n-type conductivity ensured donor centers. Under $CO+N_2$ sintering atmosphere, Schottky barriers of ZnO ceramics will be suppressed by lowering the concentration of acceptors at grain boundaries and then inducing a large increase in the Hall mobility, thereby increasing the conductivity.

The presented work concerns ZnO based ceramics. They are fabricated with doping by TiO_2 (0.50mol%), Al_2O_3 (0.25mol%) and MgO (1.00mol%) and sintering in different atmospheres (Air (A), N_2 (N), $CO+N_2$(C)). We obtained uniform, dense ceramics with ZnO as main phase and Zn2TiO4 spinel as secondary and minor phase. An important increase of the conductivity was shown for the samples A, N and C which were sintered under different atmospheres. The highest conductivity ($\sigma = 1.52\times10^5$ $S\cdot m^{-1}$) was obtained under the reducing atmosphere (CO). The role of doping was investigated in the aim to identify the local environment and valence states of the doping elements. Thus, Electron paramagnetic spectroscopy (EPR) determines the concentration of reduced Ti^{3+} ions in ZnO ceramics as function of the sintering atmospheres. The relation between conductivity and Ti^{3+} ions concentration shows opposite behavior between these parameters suggesting that Ti^{3+} ions act as traps for charge carriers. For Al ions, nuclear magnetic resonance (NMR) technique was used to identify the involved local coordination of these ions. Beyond the six and forth coordinated Al, an extra NMR line with a quite high chemical shift (185 ppm) was well resolved in all NMR spectra of samples (A, N, C) with the highest intensity in C ones. The assignment was attributed to Al ions involved in grain boundaries and supported by NMR on ball milled ceramics which show a net lowering of 185 ppm signal due to lowering the interface in nanopowders. These investigations give precise insight on the Al location in the samples, preferentially at grain boundaries contributing to increase the electrical conductivity in doped ZnO ceramics.

Poster

Electrochemistry coupled to Liquid Chromatography and Mass Spectrometry for Studying Xenobiotics Metabolism: Tools and Technologies

Ranil Clément TEMGOUA TONLEU[a,b], Renaud BOISSEAU[a], Dimitri ALVAREZ-DORTA[a], Christine THOBIE-GAUTIER[a], Ignas KENFACK TONLÉ[b], Mohammed BOUJTITA[a]

[a] *Université de Nantes, CNRS,Chimie Et Interdisciplinarité: Analyse, Synthèse et Modélisation (CEISAM), UMR 6230, 2 Rue de la Houssinière, BP 92208, Nantes, France*
[b] *University of Dschang, Electrochemistry and Chemistry of Materials, Faculty of Science P.O Box 67, Dschang, Cameroon*

Xenobiotic metabolism is a biochemical modification of (lipophilic) substances through enzymatic pathways into easily excreted (hydrophilic) metabolites. It is an important process for the detoxification of the human body from artificial poisonous compounds, namely xenobiotics [1]. Xenobiotics (from the Greek *xenos* "stranger" and *bios* "life") are artificial substances foreign to a biological system. These compounds are primarily products of human activity (environmental pollutants, drugs, food additives, etc.). They can be introduced into living organisms in many different ways - inhalation, transdermal, or orally, among others. The fate of compounds in the human body is known as ADME (Absorption, Distribution, Metabolism, and Excretion). Most xenobiotics have lipophilic character, hence it is difficult to excrete them from the body. More lipophilic substances are accumulated in cell membranes and in fat tissue. A conversion of lipophilic substances to hydrophilic products is necessary for detoxification of organisms. However, the metabolism of xenobiotics can also lead to the formation of toxic metabolites [2-4].

Therefore, the knowledge of metabolic pathways and biotransformation of xenobiotics, artificial substances foreign to the entire biological system, is crucial for elucidation of degradation routes of potentially toxic substances. Nowadays, there are many methods to simulate xenobiotic metabolism in the human body in vitro. In this poster presentation, a summary of methods used for prediction of metabolic pathways and biotransformation is described. Above all, focus is placed on the coupling of electrochemistry to liquid chromatography-mass spectrometry, which is still a relatively new technique. This promising tool can mimic both oxidative phase I and conjugative phase II metabolism. Different experimental arrangements, with or without a separation step, and various applications of this technique are presented.

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Poster

Influence of cold sintering parameters on the properties of the BCZY electrolyte material

Kawther THABET[a], Annie LE GAL LA SALLE[a], Olivier JOUBERT[a]

[a] *Institut des matériaux Jean Rouxel (IMN) CNRS UMR 6502, Université de Nantes*
2, rue de la Houssiniére, BP32229, 44322 Nantes Cedex 3, France

Sintering thermal treatment of ceramic materials used for fuel cells (SOFC) is a crucial step to densify and improve material properties. However, many sintering processes involve relatively high temperature ranges to achieve dense material. For refractory materials, the sintering temperature is typically higher than 1200 °C, and the time required to densify the material can be up to several hours. Recently, a new sintering process, named cold sintering (CSP), has been developed by Clive Randall (USA) to offer the possibility of low-temperature densification while preserving excellent properties of the material [1]. This new technique, derived from the hydrothermal method, consists on sintering materials by mixing a powder with a liquid phase, which causes a dissolution-precipitation mechanism under pressure and temperature.

In this study, the cold sintering process is applied to the electrolyte material $Ba\,Ce_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCZY). This composition belongs to solid solution between yttrium-substituted barium cerate (BCY) and yttrium-substituted barium zirconate (BZY) and exhibit both a high protonic conductivity and a good chemical stability [2]. The presented work demonstrates the feasibility of applying cold sintering to achieve dense electrolyte material BCZY a temperature < 200 °C, 6 times lower than usual. Various sintering parameters are tested to optimize material properties such as pressure, temperature, type of solvent. The first experimental observations show a significant enhancement of the densification of the material obtained by cold sintering (75 %), compared to that obtained without the addition of solvent (60 %). It has also been found that after a post heat treatment at 1200 °C the material relative density is slightly improved and reach 92 %. This result confirms very well the microstructure of cold sintered material obtained with Scanning electron microscopy.

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Poster

Calibration of the XENON1T experiment at low energies using a ^{83m}Kr source

Chloé Therreau*, Jean-Pierre Cussonneau, Sara Diglio, Julien Masbou, Dominique Thers

Subatech, UMR 6457 CNRS, IMT Atlantique, Université de Nantes, 4 rue Alfred Kastler, Nantes
*(*chloe.therreau@subatech.in2p3.fr)*

In the last century, several astrophysical observations have provided strong evidences on the existence of dark matter in the universe. This dark matter, non-luminous, and weakly interacting, could be composed of massive particles called WIMPs.

XENON1T, the third direct detection experiment designed by the XENON collaboration, consists of a dual-phase (liquid-gas) time projection chamber (TPC), filled with xenon. XENON1T is the largest TPC ever built for dark matter searches and conceived to detect an elastic scattering of a WIMP with the target nuclei. The energy transfer during such interaction induces a low energy nuclear recoil (below 100 keV).

In order to study the detector response to the energy deposit, the XENON collaboration carries out several calibration campaign with different sources. In particular, an internal source of ^{83m}Kr, which emits two radiations at low energies (32.2 keV and 9.4 keV), is used to calibrate XENON1T in the energy range where dark matter is expected.

Since data taking period dedicated to the search for dark matter lasts for several months, it is essential to monitor the detector stability and to study its response over time: regular ^{83m}Kr calibrations are carried out for this purpose.

For additional studies of the detector characteristics, the ^{83m}Kr source allows the determination of the xenon purity, the light collection efficiency and the distortion of the electric field.

Keywords: *dark matter, direct detection, XENON1T, calibration*

Poster

Influence of the processing parameters on the final properties of powder-bed laser additively oxide dispersion strengthened (ODS) Fe-14Cr steel parts

Elodie VASQUEZ[a,b], Pierre-François GIROUX[a], Fernando LOMELLO[b], Hicham MASKROT[b], Philippe CASTANY[c]

[a] *DEN-Service de Recherches Métallurgiques Appliquées, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France.*
[b] *DEN-Service d'Etudes Analytiques et de Réactivité des Surfaces, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France.*
[c] *ISCR/CM - INSA, Institut des Sciences Chimiques de Rennes (ISCR), INSA Rennes, 20 Avenue des Buttes de Coesmes, 35708 Rennes, France*

Oxide Dispersion Strengthened (ODS) ferritic steels typically contain a fine dispersion of nanosized Y-Ti-O precipitates, leading to an improvement of creep properties and neutron swelling resistance. These alloys are usually manufactured by different successive steps: mechanical alloying, outgassing, hot extrusion and cold working. Mechanical alloying aims at the dissolution of Y and Ti atoms into the ferritic matrix. This process leads to the precipitation and growth of fine Y-Ti-O oxide dispersoids during the heat treatments and the consolidation by hot isostatic pressing and/or by hot extrusion. Considering the limitations regarding the final shapes complexity of components obtained by this traditional fabrication route, the evaluation and development of alternative production methods are currently studied in order to increase the widespread use of ODS alloys.

In the frame of assessing the potentialities of additive manufacturing to manufacture ODS complex parts, a Fe-14Cr-1W + 0.3% Y_2O_3 + 0.3% TiH_2 milled powder is consolidated by Selective Laser Melting (SLM). The influence of processing parameters (scanning speed, scanning strategy, laser power, etc…) on the final microstructures as well as the final densities are studied. For this purpose, several microstructural techniques (scanning electron microscopy, electron backscattered diffraction & transmission electron microscopy) are coupled in order to analyze the cross-sections. First results are quite promising since density of more than 98% could be achieved with a non-optimized powder. As expected, processing parameters strongly influence the microstructural evolution, especially the grains size and the precipitates' density. The influence of powder properties, such as particles size distribution and flowability, on the final properties are also studied and presented in details.

The objective of this work is to demonstrate how process parameters tailor the microstructure of such alloys and so final mechanical properties.

Poster ☒

Theoretical study of the excited state intramolecular proton transfer (ESIPT) of highly emissive organic dyes

Pauline VERITE [a],

Julien MASSUE [b], Gilles ULRICH [b], Denis JACQUEMIN [a]

[a] *Laboratoire CEISAM, UMR CNR 6230, Université de Nantes, 44000 Nantes*
[b] *Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Sante (ICPEES), UMR CNRS 7515, Ecole Européenne de Chimie, Polymère et Matériaux (ECPM), Université de Strasbourg, 67087 Strasbourg*

Excited-State Intramolecular Proton Transfer (ESIPT) is a phenomenon observed in systems with an intramolecular hydrogen interaction forming, in the most of cases, an open six-membered ring. Under excitation, the hydroxy group becomes more acidic, and the nitrogen more basic twiggering the transfer from an enol to a keto form. One of the necessary conditions for the transfer is the stability of the keto product. The large difference between the geometries of the absorbing and emitting forms makes it possible to obtain a red-shifted emission and a large Stokes shift, opening the door to multiple applications in LEDs, laser dyes, logic gates, photostabilizers, and fluorescent probes. ESIPT emitters based on a 2-(2'-hydroxyphenyl)benzazole (HBX) scaffold and incorporating trialkyl- or triarylsilyl substituents at various positions have been synthesized by our partners and shown to present very bright emissions in several media. In this context, the nature of the excited states has been investigated with Time-Dependent Density Functional Theory (TD-DFT) considering toluene as solvent thanks to the use of the corrected linear-response version of the PCM approach. The obtained energies were also corrected with the second order algebraic diagrammatic construction [ADC(2)] approach. To evaluate the energetic barriers in the excited states, the transition state (TS) for ESIPT has been determined as well as the transition state leading to the conical intersection of the keto tautomer, so as to estimate both the ease of the ESIPT and the possibility of non-radiative deexcitation. Our analysis predicts a keto excited state more stable than its enol counterpart, thereby an emission from the ESIPT form, in agreement with experimental evidences. The evolution of the fluorescence wavelength with substitution is also well reproduced by theory.

Poster

Diagnostic of linear and nonlinear optical properties of some specific metallo-supramolecular thin films based on triple helicates

Karolina Waszkowska[a], Yohan Cheret[a], Abdelkrim El-Ghayoury[a],
Anna Zawadzka[b] and Bouchta Sahraoui[a]

[a] *LUNAM Universite, Universite d'Angers, CNRS UMR 6200, Laboratoire MOLTECH-Anjou,*
2 bd Lavoisier, 49045 Angers Cedex, France
[b] *Department of Automatic and Measurement Systems, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland*

ABSTRACT

This work presents studies of the linear and nonlinear optical properties of thin films containing metallo-supramolecular architectures such as triple helicates deposited by spin coating method. These studied complexes are resulting of the self-assembly process of three ligands and two metal cation (fig. 1). As a cation were chosen two metal ions such as Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} [1] to study the influence on the linear and nonlinear optical properties. These properties of the thin films were examined by using Photoluminescence, Second and Third Harmonic Generation techniques. The experimental spectra allowed us to determine the optical constants. The nonlinear optical susceptibilities of studied supramolecular complexes were measured by using the theoretical models. We also present the morphology of examined thin films by using the Atomic Force Microscopy technique.

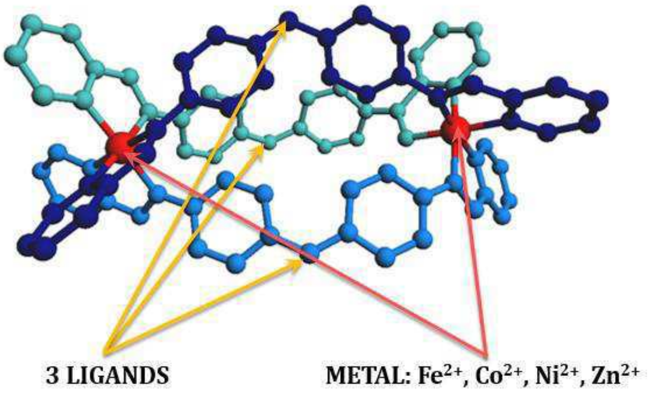

Fig. 1. Scheme described triple metallo-helicate.

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Communication Poster

Formulation and characterization of silicon-based electrodes for high energy density Li-ion batteries

Jianhan XIONG[a], Sunkyu PARK[a], Nicolas DUPRÉ[a], Lionel ROUÉ[b], Michel ULLDEMOLLINS[c], Dominique GUYOMARD[a], Bernard LESTRIEZ[a]

[a] *Institut des matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, 44322 Nantes, France*
[b] *INRS- Energie, Materiaux, Telecommunications, Varennes, Quebec, J3X 1S2, Canada*
[c]*SAFT, 111-113 Boulevard Alfred Daney, 33000 Bordeaux, France*

In need of increasing automotive applications, it is necessary to find both higher capacity and higher-capacity retention electrode materials for Li-ion batteries. Silicon is a promising negative electrode active material for lithium-ion accumulator due to its high theoretical specific capacity (3579mAh.g^{-1}) [1]. However, the main challenge to realize the commercialization of this material as a negative electrode remains its excessive irreversible capacity during cycling. Indeed, during lithiation, the material undergoes a huge volumetric expansion up to 280%, causing a progressive mechanical degradation that promotes a continuous growth of the layer SEI (Solid Electrolyte Interphase) [2, 3]. In order to minimize the volume variations, optimizing the silicon-based electrode formulation and understanding the electrode failure mechanism are crucial to solve the problem of low coulombic efficiency and capacity fading.

This project aims at increasing the energy density of Li-ion batteries to 700Wh/L using a full cell level approach. Hence, we propose a solution by using a 1:1 silicon-graphite mixture as active material to reduce the variation of the average volume of the electrode while keeping an attractive energy density.

A typical negative electrode of Lithium-ion battery is made of the active material, which is mixed with carbon-conductive additive and polymer binder to retain it in good electronic and mechanical conditions. Firstly, the electrode formulation is optimized by various parameters, especially the ratio of the carbon-conductive additive and the polymer binder. Then, a mechanical processing on the electrode seems necessary, in particular the calendering and maturation [4]. These two steps provide a beneficial effect on electronic and ionic conduction as well as mechanical properties within the materials. Analysis of the electrode morphology as well as electrical resistivity, peel adhesion test and electrochemical performance measurements are the principal techniques to evaluate the studied formulations. ^{7}Li and ^{19}F MAS-NMR characterization allow quantifying the lithium and the fluorine trapped in the SEI layer and following its formation and evolution during the electrochemical cycling according to the parameters of electrode preparation.

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