# liten

RAPPORT SCIENTIFIQUE
SCIENTIFIC HIGHLIGHTS 2013

liten

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DE LA RECHERCHE À L'INDUSTRIE

cea

# Éditorial
# *Foreword*

## LE LITEN ORIENTE SES ACTIVITÉS DE RECHERCHE ET DÉVELOPPEMENT VERS L'INNOVATION TECHNOLOGIQUE POUR ACCOMPAGNER LA TRANSITION ÉNERGÉTIQUE ET CULTIVE L'EXCELLENCE SCIENTIFIQUE

Les activités de R&D conduites à l'institut LITEN du CEA Grenoble concernent les nouvelles technologies pour les énergies à faible empreinte carbone. Avec 135 nouvelles publications de rang A, 235 brevets déposés, 30 thèses soutenues et 6 nouvelles habilitations à diriger les recherches (HDR), l'institut a poursuivi en 2013 sa politique de ressourcement scientifique pour accompagner au meilleur niveau les développements technologiques pour l'industrie qui constituent sa vocation première. Le LITEN a su tisser et cultiver des partenariats privilégiés avec des laboratoires académiques tant nationaux qu'européens pour réaliser des recherches de qualité dans chacun des thèmes que nous abordons, depuis les nanomatériaux jusqu'aux réseaux d'énergie. Un florilège des meilleurs résultats obtenus en 2013 avec nos partenaires est présenté dans ce rapport scientifique qui vous donnera je l'espère envie de collaborer avec le LITEN.

## *AN R&D PROGRAM CENTERED ON TECHNOLOGICAL INNOVATION TO SUPPORT ENERGY TRANSITION AND CULTIVATE SCIENTIFIC EXCELLENCE*

*The R&D activities being developed at the LITEN institute in CEA Grenoble are centered on the development of new technologies for low carbon energies. With 135 new publications in high impact factor journals, 235 patents applications, 30 PHD thesis defended and 6 new "habilitations" to supervise PHD research (HDR, the highest research diploma in France), the LITEN institute continued, in 2013, to focus on scientific resourcing in order to meet the demands of industry at the highest technological level – a policy which remains at the top of the institute's agenda. The LITEN institute has established privileged partnerships with academic laboratories, both at national and European level. These partnerships have been especially selected to complement our own core research areas and cover themes as diverse as nanomaterials to energy grids. An anthology of the best results obtained in 2013 with our partners is presented in the Scientific Report, which I hope will encourage you to collaborate with us in the future.*

**Florence Lambert**
Directrice du Liten
*Head of liten*

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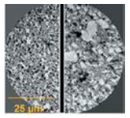
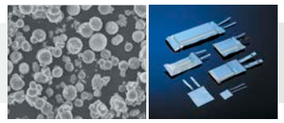

X rays Nanotomography of ceramic cells

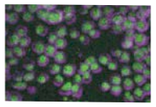

PEMFC system

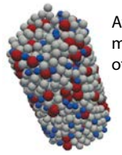

Alsolen: 500 KW Fresnel Concentrated Solar Power


Powder for batteries


Solar cells


Integration of CEA technologies 15 KWh Li Battery + 25 kW PEMFC + 10,5 kg $H_2$ ~ 350kWh


Fuel cell catalyst


Atomic scale modelling of hydrides


Battery cells


Solar recharging station with local micro-grid

L'institut LITEN conduit des activités de R&D centrées sur le développement des nouvelles technologies pour l'énergie. S'inscrivant pleinement dans la démarche de transition énergétique, le LITEN oriente ses travaux vers la diversification de vecteurs énergétiques à faible empreinte carbone et le développement de technologies de production, stockage et conversion de ces vecteurs. L'efficacité énergétique et l'efficacité matière sont au centre des recherches qui couvrent toute la chaine de la valeur depuis le développement de matériaux et leur mise en œuvre dans des composants, eux même intégrés dans des systèmes et validés en situation représentative d'un fonctionnement réel.

Les recherches à caractère finalisé conduites au LITEN sont destinées aux transferts technologiques vers le tissu industriel. A cette fin, l'institut couvre une large gamme de TRL (Technology Readiness Level) lui permettant de passer de la preuve de concept à l'échelle du laboratoire au prototype préindustriel. Une attention majeure est accordée au retour d'expérience issu des démonstrateurs. L'analyse de leur comportement en situation réelle et la mise en œuvre de nombreuses techniques de caractérisation complémentaires et parfois sophistiquées (in situ, operando, grands instruments) permettent d'identifier les mécanismes limitant leurs performances ou leur durée de vie, d'améliorer le concept de base, de définir les essais accélérés pertinents ou de cibler le paramètre à mesurer et contrôler durant le fonctionnement.

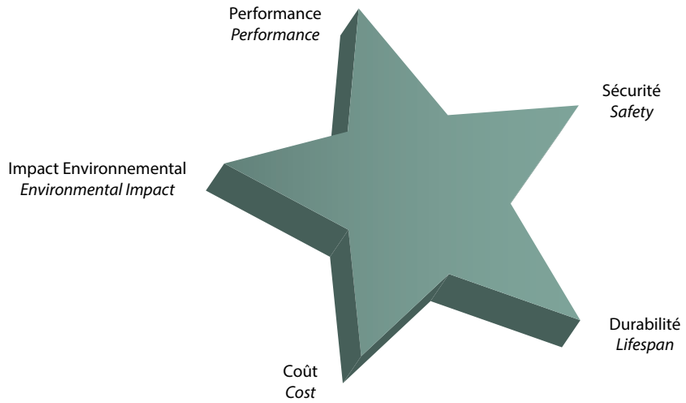
*The LITEN institute is a major driver of R&D activities centred on the development of new technologies for renewable energy. Liten aims to become a major technological contributor to the energy transition, and its strategic focus is oriented towards the diversification of low-carbon energy vectors and the development of technologies for producing, storing and converting them. Energy and materials efficiency constitute the main core of its research activities which cover every level of the entire value chain from the development of materials designed and processed specifically for components that are integrated into systems and validated in live, representative conditions.*

*The results of LITEN's applied research are ultimately destined for technological transfer towards industry. To this end, the institute covers a wide spectrum of the "Technology Readiness Level" (TRL) criterias and is involved in the development of every level from laboratory sized proof of concept to pre-industrial prototyping. Particular attention is paid to feedback acquired from tested prototypes. The analysis of such behaviours, in real life conditions, and the use of multiple, complementary and sometimes sophisticated characterization techniques (in situ, operando, large facilities) enables the identification of mechanisms that have a limiting effect on performance and lifespan. Moreover, such data are used to improve design concepts, to define accelerated tests, or identify the relevant parameters that need to be measured and controlled when running a prototype.*



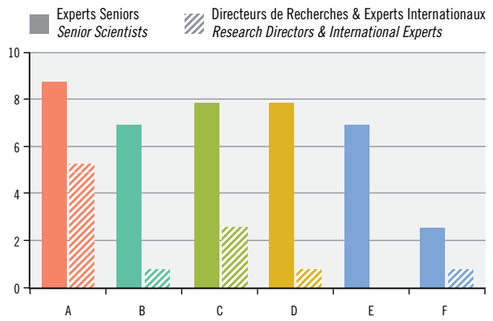
Pour toutes les technologies étudiées ou développées, on cherche à optimiser le triptyque classique « performance, durabilité et coût » auquel viennent s'ajouter les critères sécurité et impact environnemental.

*Liten has complemented the traditional tripartite approach which covers « performance, durability and cost optimisation" by adding additional criteria such as safety and environmental impact to all of its research activities.*

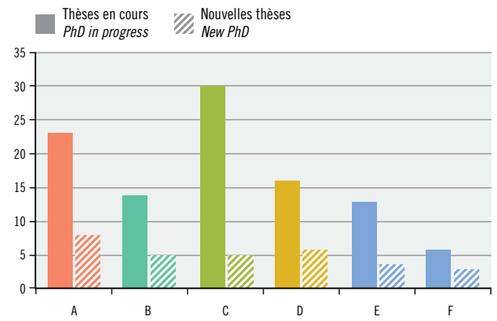



Pour cultiver son excellence scientifique et technologique le LITEN s'appuie sur une démarche continue de ressourcement de ses équipes, de ses moyens expérimentaux et de ses plateformes d'essais ou de prototypage. Dans cette optique une attention particulière est portée aux habilitations à diriger les recherches (HDR). En 2013, 6 nouvelles habilitations ont été obtenues portant à 25 le nombre de détenteurs d'une HDR au LITEN.
La démarche de ressourcement s'organise principalement autour du réseau des 60 experts seniors, experts internationaux et directeurs de recherche du LITEN. Elle s'appuie sur des partenariats académiques nationaux et internationaux privilégiés, cultivés dans la durée, et se concrétise par des projets de recherches institutionnels communs ANR (60) et Carnot (30) ou Européens (120 FP7). Les thèses et post-doctorats sont au cœur de cette démarche. En 2013 le LITEN a accueilli une centaine de doctorants et 30 post-doctorants.

*In order to raise the quality of its scientific and technological research, LITEN looks to constantly improve the resourcing of its scientific teams, its technological equipment and infrastructure and its testing/prototyping platforms. In this respect, particular attention is paid to the "Habilitation for Research Direction" HDR diploma, which enables researchers to supervise PhD research. In 2013, 6 new HDR grades were obtained, increasing to 25 the number of LITEN credited scientists .*
*The scientific and technological resourcing approach within LITEN is based on a structured network of 60 senior scientists, international experts and research directors. It relies on many long-term national and international academic partnerships embodied through a wide variety of common institutional research projects funded either by the French National Research Agency ANR (60 and 30 Carnot) or the European framework (120 FP7). PhD students and post-doctorate scientists lie at the heart of this approach. In 2013, 100 PhD students and 30 Post-doc scientists carried out their research at LITEN.*



Distribution thématique des experts au LITEN
*Expert thematic distribution within LITEN*



Distribution thématique des thèses au LITEN
*Thematic distribution of PhD thesis within LITEN*

A. Matériaux (nano), Micro sources d'énergie et Procédés – B. Conversion thermochimique de la biomasse, Production de vecteurs énergétiques hydrogène et biogaz – C. Composants et systèmes solaires photovoltaïques (inorganique et organique) et thermiques – D. Batteries et Piles à Combustible pour la mobilité – E. Intégration et stockage des énergies renouvelables par une approche « smart energy grids » – F. Efficacité énergétique dans le bâtiment et l'industrie.

*A. Materials (nano), micro energy sources and industrial processes – B. Thermochemical conversion of biomass, Production of energy carrier's hydrogen and biogas – C. Components and systems for solar photovoltaic (inorganic / organic) and solar thermal applications – D. Batteries and fuel cells for transport applications – E. Integration and storage of renewable energy sources via a "smart energy grid" approach – F. Energy efficiency for buildings and industry.*

# L'activité scientifique au LITEN en 2013

Une **sélection de résultats scientifiques marquants de l'année 2013** représentatifs des grands thèmes de R&D de l'institut est présentée dans la suite ce document. Ils ont pour la plupart été obtenus en partenariat avec d'autres unités du CEA ou avec des partenaires académiques.

## MATÉRIAUX, MICRO SOURCES D'ÉNERGIE ET PROCÉDÉS

L'activité **matériaux** au LITEN a notamment concerné en 2013 le développement de nanomatériaux pour modifier des propriétés telles que la conduction thermique d'une paroi ou la viscosité d'un liquide. Elle a inclu également la fonctionnalisation de surfaces par intégration de nanotubes de carbone ou de nanofils d'argent. De telles approches ont également été mises en œuvre pour le développement de **micro-sources** d'énergie telles que les générateurs thermoélectriques. Un effort important a été consacré à l'amélioration des **procédés** de mise en œuvre des matériaux pour augmenter leur efficacité matière, baisser les coûts, tout en maintenant le niveau de performance des pièces produites. Enfin L'étape de recyclage des composants pour l'énergie a également commencé à être appréhendée.

## SOLAIRE PHOTOVOLTAÏQUE ET THERMIQUE

**L'énergie solaire photovoltaïque et thermique** occupe un rôle privilégié dans la transition énergétique et une part croissante dans les mix énergétiques mondiaux. Pour baisser encore le coût du kWh électrique ou thermique et augmenter la durabilité des systèmes les recherches LITEN en 2013 ont notamment porté sur le contrôle de la pureté du silicium, l'analyse des défauts rédhibitoires pour l'efficacité des cellules, le développement de matériaux et de cellules alternatifs et l'analyse des mécanismes de dégradation à l'échelle du matériau et des composants.

## BATTERIES ET PILES À COMBUSTIBLE POUR LA MOBILITÉ

**Les piles à combustible et les batteries** constituent une réponse technologique très pertinente pour le développement d'une mobilité à faible empreinte carbone dont le déploiement reste timide en France. L'un des verrous au développement des piles à combustible dans les transports provient de l'utilisation du catalyseur de platine. Pour y remédier, le LITEN a engagé en 2013 diverses approches pour diminuer la teneur en platine des piles à combustible tout en maintenant leur niveau de performance. Les batteries actuelles souffrent encore d'une dégradation significative de leurs performances lors des cycles charge-décharge. En comprendre l'origine pour proposer des remèdes est resté une des priorités du LITEN en 2013, tout comme l'augmentation de la capacité des batteries et de leur niveau de sécurité. Ces recherches ont été conduites au niveau des matériaux, des cellules élémentaires et des prototypes de laboratoire. Le retour d'expérience après intégration et fonctionnement en système réel permet de préparer les transferts technologiques mais également de redéfinir les axes de recherches pour améliorer les points faibles des composants.

## BIOMASSE, HYDROGÈNE ET BIOGAZ

Un des enjeux dans la conversion de la **biomasse** est d'élargir la ressource valorisable tout en gardant un bon rendement carbone, énergie et coût sur le cycle complet. Les recherches conduites au LITEN en 2013 ont visé notamment la compréhension et le contrôle de la formation de sous-produits lors de l'étape de conversion en fonction de la composition de la ressource ainsi que l'utilisation de l'humidité de certaines biomasses dans le procédé de conversion pour en augmenter l'efficacité. L'augmentation du rendement de conversion de la biomasse peut aussi faire intervenir l'ajout d'hydrogène, également étudié comme vecteur énergétique à faible empreinte carbone. La production d'un tel **hydrogène** avec une efficacité et un coût compatible avec le marché actuel est restée au cœur des développements LITEN sur l'électrolyse de l'eau en 2013. Le stockage sûr de l'hydrogène a également été appréhendé afin de proposer une expertise et des innovations sur toute la chaine de la valeur de l'hydrogène-énergie.

## RÉSEAUX ÉLECTRIQUES, STOCKAGE ET EFFICACITÉ ÉNERGÉTIQUE

L'intégration des énergies intermittentes telles que l'énergie solaire dans **les réseaux électriques,** dans les réseaux de chaleur ou dans les bâtiments passe par des développements spécifiques en électronique de puissance et en génie électrique associés à la maitrise des systèmes de **stockage de l'énergie** (batteries, chaine hydrogène, stockage de la chaleur). Les expérimentations à échelle représentative et la modélisation conduites au LITEN en 2013 constituent une étape clé pour éprouver et valider les solutions énergétiques pertinentes de demain.



# *LITEN Scientific Activity in 2013*

*The following is a **selection of scientific highlights from 2013,** representative of LITEN's core areas of research. They have been obtained, for the most part, in collaboration with other CEA units or with academic partners.*

## *MATERIALS, MICRO ENERGY SOURCES AND INDUSTRIAL PROCESSES*

*Activities relating to **materials** in 2013 particularly concerned the development of nanomaterials to modify properties such as wall thermal conduction or liquid viscosity. The addition of functionalities to material surfaces using carbon nanotubes or silver nanowires have also been studied. A similar approach has been adopted for the development of **energy microsources** such as thermoelectric generators. A major effort has been dedicated to the improvement of **material processes** in order to increase the efficiency of materials and reduce costs whilst maintaining the performance levels of components being manufactured. Liten has also started to study the recycling stage of these energy components.*

## *SOLAR ENERGY: PHOTOVOLTAIC AND THERMAL*

***Solar energy, (photovoltaic and thermal),** is a major component of the energy transition with an increasing share of the world energy mix. In order to decrease the cost per kWh of solar electricity or heat and to increase the system's durability, LITEN's R&D in 2013 has focused on the control of silicon purity, the analysis of unacceptable defects that will affect cells' efficiency, the development of alternative materials and cells and the analysis of the degradation mechanisms at a material and component scale.*

## *BATTERIES AND FUEL CELLS FOR MOBILITY*

***Fuel cells and batteries** are highly relevant technological solutions for a low carbon electromobility applications despite their limited deployment in France. The use of platinum catalysts in fuel cells is one factor limiting their deployment in vehicles. LITEN has consequently worked on several approaches in 2013 aimed at reducing the platinum content of fuel cells whilst maintaining their performance levels. Current batteries still suffer from significant decreases in performance relating to charge-discharge cycles. Understanding the mechanisms responsible for such issues and developing solutions remained key priorities for LITEN in 2013, as well as working on increasing battery capacity and safety. These R&D activities have been carried out at a material scale, on single cells and on laboratory prototypes. The feedback gained after their integration in full size systems and real-life operations allows LITEN to prepare the transfer of technology towards industry, but also to fine-tune key research areas relating to components' weak points that need to be improved.*

## *BIOMASS, HYDROGEN AND BIOGAS*

*One of the major challenges in the conversion of **biomass** relates to the broadening of the feedstock to be exploited whilst ensuring a good efficiency over the complete cycle in terms of carbon, energy and cost. In 2013, this research topic focused on understanding and controlling the formation of by-products during the conversion stage of various feedstock, or at taking advantage of the moist content of certain biomass materials in the conversion process to increase its efficiency. Increasing the efficiency of the conversion of biomass can also result from the addition of hydrogen into the process. **Hydrogen** is studied at LITEN as a low carbon footprint energy vector. The production of such hydrogen with efficiency and cost conforming to current accepted market prices has remained a major R&D topic in LITEN in 2013, in particular in the field of electrolysis. Similarly, a secure means of hydrogen storage has been studied allowing LITEN to offer high value expertise and innovations across the entire hydrogen-energy value chain.*

## *ELECTRICAL NETWORKS, STORAGE AND ENERGY EFFICIENCY*

*The integration of intermittent energy sources such as solar energy into the **electric grid,** into heat networks or into buildings necessitates specific developments in power electronics and in electrical engineering linked to the control of **energy storage** systems (batteries, hydrogen chain, heat storage). The experiments made at representative scale and the modelling activities carried out at LITEN in 2013 are an essential step in evaluating and validating relevant energy solutions for the future.*

# Matériaux, Micro sources d'énergie et Procédés
# *Materials, micro energy sources and industrial processes*

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## « HABILITATIONS À DIRIGER DES RECHERCHES »

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## THÈSES / *PHD*

- **Vincent DUBOIS (DTNM) :** Electrodes lithiées pour microbatteries lithium-ion – 03/10/13
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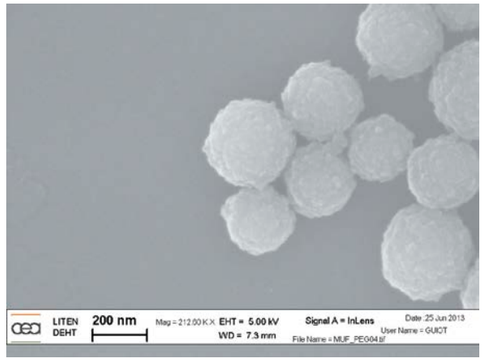
# Nanofluids with encapsulated phase changed materials nanoparticles for enhanced heat transfer





## SUMMARY

**In order to increase the thermal conductivity of synthetic oils used as high temperature heat transfer fluid, core-shell nanoparticles of encapsulated phase change materials (PCM) have been produced and characterized. They are likely to increase the thermal energy storage capacity through the latent heat of solid/liquid transition.**


## CONTEXT

Currently synthetic oils used as high temperature heat transfer fluid in concentrated solar power plants have low thermal conductivity and limited thermal energy storage. The idea behind this project is to improve thermal performances by adding nanoparticles as shown by S. Choi in J. Heat Transfer 2009.

## APPROACH

Nanometer-sized PCMs have significant advantages compared to micron sized encapsulated PCMs. They have higher effective heat capacity due to their higher phase change efficiency and they are less restrictive to flow. Our target in this work was to design core-shell nanoparticles in the 100 to 400nm range integrating a PCM core.
To be really efficient, such core-shell nanoparticles have to exhibit several key properties. The nanoparticles must survive numerous thermal cycles during the whole life time of the heat transfer fluid (at least 15 years for synthetic oils used in CSP plants!). In addition, the shell has to be robust enough to absorb the volume change occurring upon solid/liquid transition. Nanoparticles have also to be robust enough to withstand pumping at high flow rate. To increase the thermal transfer between the oil and the PCMs core, the shell has to exhibit a good thermal conductivity. Finally, the supercooling of the PCMs encapsulated inside the nanoparticle has to be strictly controlled by tuning the inner surface of the shells. This is done by grafting nucleation site.


## TEAM

Jonathan Skrzypski, Stéphane Mossaz, Anton Gruss, Philippe Berne, Olivier Poncelet

## CONTACT

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## RESULTS

We concentrated our effort first on the production of the shell. Melamine-urea –formol materials (MUF) were selected due to their high thermal stability (over 400°C) and their high chemical inertness versus both the synthetic oil and PCMs (metals, organic or mixtures of salts). The growth of the shells is made by both classical micellar or reverse micellar synthetic pathways depending on the nature of the PCMs. A typical nanoparticule 100nm diameter is presented in figure 1. The shell thermal conductivity can be increased by adding nano sheets of hexagonal boron nitride during the growth of the shells around the PCMs as illustrated in figure 2.
Before being integrated in oils, they have been integrated and tested in water. Preliminary results assess the robustness of the particles and show that thermal conductivity reaches a satisfactory level and is increased by adding hBN sheets.

## CONCLUSIONS AND PERSPECTIVES

Highly stable core-shell nanoparticles of encapsulated PCMs have been produced, characterized and preliminary evaluated. The next step is to integrate these particles in the real oil.


## FUNDING

This project was carried out as part of a Carnot program (SOLARNANO; Energies du Futur)



**References**

[1] Ribeiro J.P, Gruss J.A. Nanofluides pour les applications thermiques, Dossiers techniques de l'ingénieur. 2009

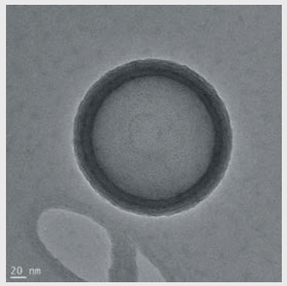




**Fig. 1**
Core-shell nanoparticles
(PCM is anthracene, Shell is MUF)

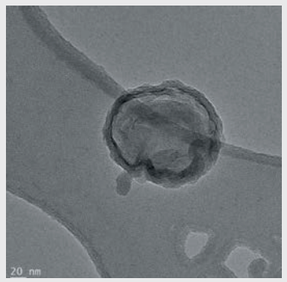
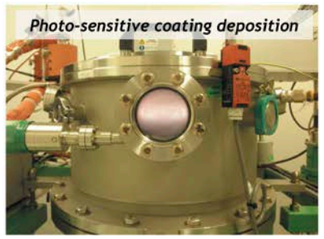
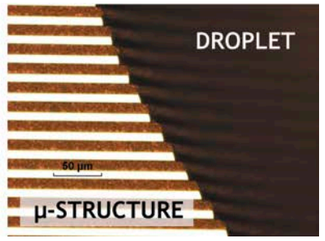



**Fig. 2**
Core-shell nanoparticles (PCM is anthracene, Shell is MUF. Some hBN nanosheets cross the shell.

# Anisotropic and biomimetic surfaces to enhance spontaneous liquid displacement



## SUMMARY

**Spontaneous motion of droplets due to a gradient in surface energy presents many different potential applications (inkjet printers head; water drainage; and heat transfer improvements). Biomimetic surfaces in the field of wettability are usually studied for super-hydrophobicity (self-cleaning, non-fogging functions). Nowadays, new properties are expected to obtain a spontaneous liquid transport. Specific structures and energy gradients could even allow droplets climbing on a vertical substrate.**


## CONTEXT

Surface topologies in the natural world are surprising and can have huge impact on wettability. The well-known lotus leaf has omni-phobic properties (water/oil repels) that allow self-cleaning (rolling motion of water droplets which capture dirt). On the other hand peat moss, when dry, has a sponge-like structure that allows water spreading and absorption (hydro-philic properties). Other topologies can manage not only the wettability but also the droplet motion, such as duck feathers, rice leaves and so on… They have the ability to "choose" the droplet motion direction. Presently numerous efforts are being carried out to understand and reproduce these natural behaviours, in order to improve the surface properties of materials.

## NEEDS

Among the applications, two of them are particularly interesting. A large improvement in heat transfer at small scale can be achieved by using surface energy gradients. Guidance in the vertical direction can be useful to drive and transport liquids in microsystems.

## APPROACH

Anisotropic surfaces, with parallel rectangular grooves (width = 10 µm, height = 400 – 2000 nm) were produced by lithography and etching (Fig 1, steps 1 to 4). Then, a UV-sensitive coating (100-150 nm) was deposited (Fig 1, step 5). Finally, the surface energy gradient was obtained by selectively exposing the structure steps by steps to different UV doses (Fig 1, step 6).

## RESULTS

This selective exposure (step 6) allows realizing surface gradients on smooth or anisotropic surfaces. Nevertheless, the droplet displacement length was always increased using the anisotropic surfaces. This is due to a confinement effect related to the energy barriers caused by the µ-grooves structure that restricts the droplet spreading in grooves perpendicular direction. In this situation, the droplets also have an anisotropic shape (Fig. 2). Compared to a circular shape, this anisotropic droplet shows a higher energy gradient and it displacement is enhanced.

The best results was obtained for a structure with µ-groove depth between 1-2 µm. In this case, the droplets moved uphill on vertical surfaces at a peak velocity of 7mm/s (Fig. 3).

## CONCLUSIONS AND PERSPECTIVES

This type of function will be improved and implemented in devices for thermal management or fluidic applications.


**References**

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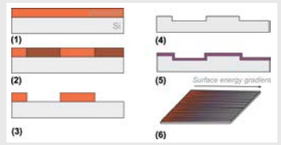


**Fig. 1**
Schematic process flow

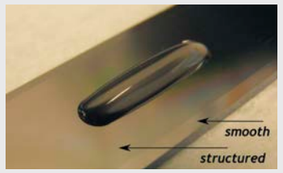


**Fig. 2**
Anisotropy – horizontal spreading of a12 µL droplet (Substrate width = 12 mm)

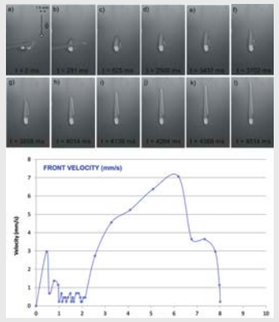


**Fig. 3**
(a) Droplet climbing
(b) Velocity versus travelled distance


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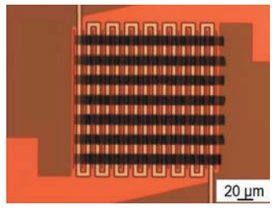
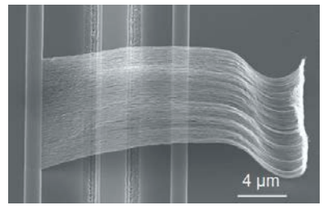
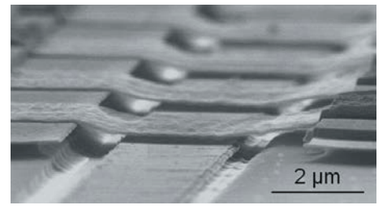
# Wafer-scale integration of suspended CNT membranes for multi-criteria gas sensor devices.





## SUMMARY

**Fully integrated gas sensor devices using suspended carbon nanotubes (CNTs) membrane are developed. These sensors are able to make gas detection by measuring the resistivity change of the membrane and the resonance frequency change induced by gas adsorption on CNTs. Gas selectivity is improved by playing with the nature of the top metal contact. These devices are also an electrical platform to test the CNT electrical performances according to the technology in use.**


## CONTEXT

Carbon Nanotube (CNT) devices are made at a temperature which normally exceeds temperature withstood by conventional CMOS technology. However, while the sensitivity of CNT based gas sensors is very good, their selectivity is rather poor. To overcome these limitations a specific CNT based technology has been developed.

## APPROACH

To overcome the problem of selectivity, a multi-criteria CNT gas sensor has been integrated. This device uses horizontal membranes made of a dense CNT array, contacted to top metallic electrodes to characterize resistance shift and suspended above an actuation electrode to allow frequency shift measurements. This MEMS device is achieved via a specific process flow with a rational choice of materials in order to perform localized horizontal and selective in-situ CNT growth by chemical vapour deposition (CVD) [1]. The integration scheme is compatible with full wafer processing and with the realization of CNT based sensors on a Si interposer with Through Silicon Via (TSV) that ultimately will be hybridized on the CMOS component.

## RESULTS

The developed process flow is highly robust and reliable. Thanks to CNT growth understanding, the integration yield of functional membranes is now higher than 90% on 100 mm wafers. The characterizations of resistive devices based on supported CNT membranes show very reproducible gas detection characteristics at the wafer-scale. When exposed to different gases, resistance shifts of a few % or no response are demonstrated, depending on the nature of the top contact electrodes (Fig. 1). This is a real asset towards selective gas detections.

## CONCLUSIONS AND PERSPECTIVES

These results are very promising and demonstrate that wafer-scale integration of CNT components becomes a reality. The components are also very interesting for others applications than sensors and constitute a unique electrical platform to study the impact of process steps like CNT cleaning, doping or encapsulation (Fig. 2) that may change the electrical performances of carbon nanotubes.

## PARTNERSHIP

EPFL, SIEMENS


## FUNDING

This work was partly carried out in the frame of a FP7 European program (e-BRAINS).



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**References**

[1] Guerin H. *et al., Microelectronic Eng.* 97 (2012) 166-8

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| Gases | Top metal | | |
|---|---|---|---|
| | Pt | Pd | Au |
| $H_2$ | | + | 0 |
| Ethanol | + | 0 | 0 |
| Toluene | 0 | 0 | |
| $NH_3$ | + | + | + |
| $H_2O$ | + | + | 0 |

**Fig. 1**
Sensor resistive responses to different gases (several ppm to 1000 ppm) depending on the nature of the top electrodes (shift up:+ , shift down:-, no shift: 0).

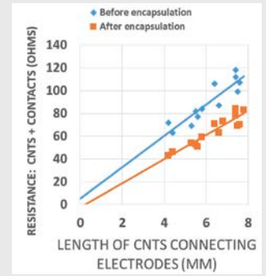
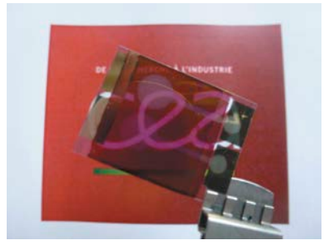
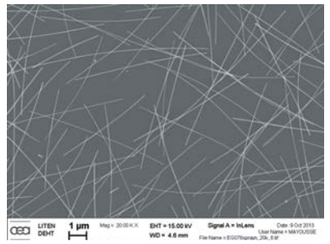



**Fig. 2**
Devices based on supported CNT membranes with Cr/Al top electrodes. Evolution of device resistances as a function of CNT lengths between the electrodes, before and after encapsulation by conformal CVD $SiO_2$

# Silver nanowire based electrodes for flexible, TCO-free OPV devices






## SUMMARY

**We present here the development of a TCO-free, fully solution-processed organic photovoltaic device incorporating silver nanowire networks. We have manufactured inverted semi-transparent polymer solar cells exhibiting power conversion efficiencies that are comparable to devices incorporating transparent conductive oxide bottom electrode and opaque silver top electrode.**


## CONTEXT

Transparent conductive thin films are widely used in technologies like light-emitting diodes, display technologies and solar cells. The manufacture of transparent conductive films is currently realized with thin films of transparent conductive oxides (TCOs). They suffer from limitations like cost of production and brittleness. The use of solution-processable silver nanowires (AgNWs) appears as a promising alternative since it affords a large area, low-cost additive deposition method for customized printable pattern with high performances [1].

## APPROACH

The silver nanowires are synthetized and then spray-coated onto plastic substrates reaching excellent conductivity at high transparency. The AgNWs were first integrated into organic photovoltaic (OPV) devices in inverted architecture. Afterwards, AgNWs were also sprayed in replacement of silver top electrode to form a semi-transparent device.

## RESULTS

Thanks to the use of spray coating, AgNW based flexible electrodes with excellent performances (i.e. R□= 17 Ω/□ at T=91%) comparable to TCO substrate, are obtained on large areas (Fig. 1). By improving the purification of the reaction mixture, applying pressure on the AgNWs and optimising the thickness of the electron transport layer, inverted OPV cells with AgNWs networks as bottom electrode or top electrode have been successfully made. Performances are similar to the ones obtained with TCO and silver electrode with PCE efficiency around 3% (Fig. 2). Furthermore AgNW based OPV cells maintain their performances after one month under continuous AM 1.5, 1000 W/m² illumination.

## CONCLUSIONS AND PERSPECTIVES

AgNWs is a very promising low cost nanomaterial based alternative for the elaboration of flexible transparent conductive films by additive processing for the production of large, flexible and semi-transparent OPV devices. Development of this architecture on OPV modules is currently ongoing. In parallel we are also doing a benchmark of TCO-free materials commercially available.


## FUNDING

This work was carried out thanks to the NTE Program CEA grant (COCON).


**Please note**

This work is done as part of the Post-Doctoral contract of Tristan Lescouet. This work was awarded at the Technoparade 2013 conference.


## TEAM

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**References**

[1] D. Langley, G.Giusti, C. Mayousse, C. Celle, D. Bellet, J.-P. Simonato, *Nanotechnology*, vol. 24, pp. 452001, 2013

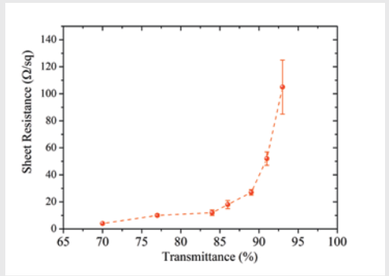




**Fig. 1**
Sheet resistance as a function of transmittance obtained with spray-coated AgNWs on flexible plastic substrate.

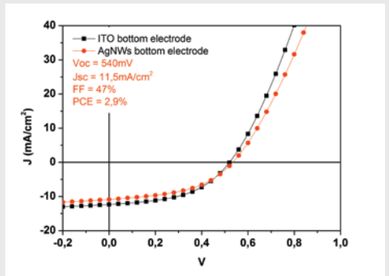
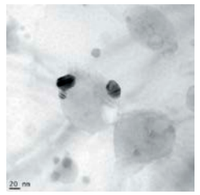
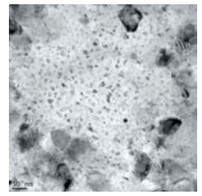


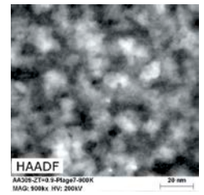

**Fig. 2**
Current density-voltage (J-V) curves of ITO bottom electrode reference cell (black square) and AgNWs bottom electrode OPV cell (red round).

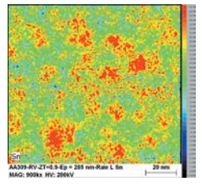


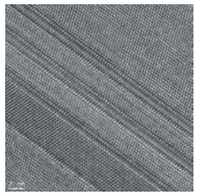
# Development of efficient thermoelectrical materials in the mid and high temperature ranges by a nanostructuration approach










## SUMMARY

**The perfect control of the sintered microstructure of a polycrystalline thermoelectrical material is the key to optimize the dimensionless figure of merit. Nanostructuration is shown as an effective way in optimizing this critical parameter.**


## CONTEXT

Thermoelectric materials have the ability to directly convert temperature differences to electric voltage and vice-versa. By properly doping, N-type (majority carriers are electrons) and P-type (holes are majority carriers) thermoelectric materials are achievable. The dimensionless figure of merit ZT ($Z = S^2\sigma/\lambda$ where S is the Seebeck coefficient, σ the electrical conductivity, $S^2\sigma$ the power factor, λ the thermal conductivity being the sum of the electronic and lattice contributions; T is the absolute temperature) is characterizing the efficiency of a thermoelectric material. The higher the ZT value, the better the thermoelectric behavior for a given material.

## APPROACH

In comparison to a monolithic material, theoretical calculations have shown that a small volume fraction of a nanometer-size second phase, homogeneously dispersed in the microstructure of a sintered polycrystalline material, leads to a drastic reduction of the lattice thermal conductivity without affecting the power factor [1]. Then a strong increase of the ZT parameter is predicted [1].
N-type $Si_{92}Ge_{08}$ [2] and $Mg_2Si_{0.4}Sn_{0.6}$ [3] alloys have been prepared by mechanical-alloying followed by Spark Plasma Sintering. The silicon-germanium alloy, interesting for applications above 550°C, has been nanostructured by an ex-situ (a second phase is incorporated) formation of a tailored volume fraction of metal-silicide inclusions during sintering. The magnesium-silicon-tin alloy, devoted to applications in the range 200-500°C, has been nanostructured by tailoring an intensive in-situ (no second phase added) precipitation during the sintering step.

## RESULTS

For both materials the formed inclusions/precipitates have a nanometer-size character (average diameter around 30 and 14 nm and concentrations are $7.4x10^{-6}$ and $1.9x10^{-3}$/nm² for the $Si_{92}Ge_{08}$ and $Mg_2Si_{0.4}Sn_{0.6}$ alloys, respectively). Fig. 1 shows the precipitates that formed in-situ when tailoring the sintering parameters of the N-type $Mg_2Si_{0.4}Sn_{0.6}$ alloy. Fig. 2 shows the drastic influence on the ZT parameter of the nanostructuration effect for both investigated alloys. Similar results have been observed on P-type $Si_{92}Ge_{08}$ [2] and $MnSi_{1.77}$ [4] alloys.

## CONCLUSIONS AND PERSPECTIVES

Nanostructuration (in-situ and ex-situ) is an effective method to increase the ZT parameter of a given thermoelectrical material. This approach will be applied to manufacturing processes enabling tens/hundreds of kilograms of powder to be produced per batch.


## PARTNERSHIP

HotBlock OnBoard



## TEAM

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**References**

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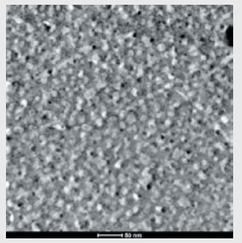


**Fig. 1**
STEM/HAADF image showing an in-situ precipitation in an N-type $Mg_2Si_{0.4}Sn_{0.6}$ alloy

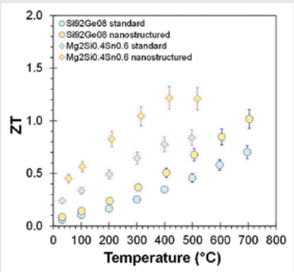
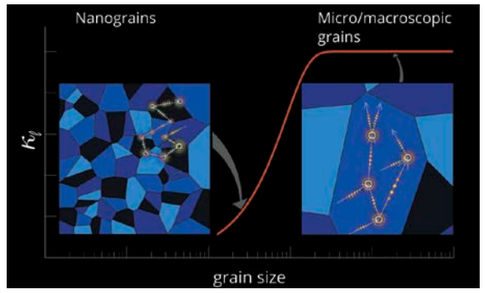
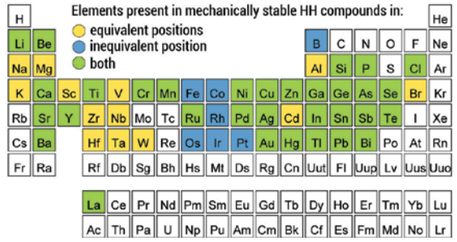



**Fig. 2**
ZT parameters in function of temperature for different N-type thermoelectrical materials tailored using the nanostructuration approach

# Screening of hundreds of compounds for thermoelectric energy conversion





## SUMMARY

**To identify new good thermoelectric materials, we used high-throughput (HT) computational pre-screening through the over 79,000 half-Heusler entries of the aflowlib.org database, identifying a dozen of these materials likely to have thermal conductivities κ< 3Wm$^{-1}$K$^{-1}$. We also computationally investigated the merit factor ZT of these compounds in the small grain limit. For many of them, ZTs are calculated to be markedly above those of nanograined IV and III-V semiconductors, and around 15% of them may outperform ZT=2 at high temperature.**


## CONTEXT

Discovering good thermoelectric materials, particularly those with very low thermal conductivities κ remains an experimental challenge due to the high costs and time-consuming synthesis procedures. For drastically reducing the set of candidates, high-throughput (HT) computational pre-screening has been shown to be a fast emerging area of materials research highly valuable [1]. We have carried out a HT investigation of lattice thermal conductivity and thermoelectric figure of merit of half-Heusler compounds for the first time [2].

## APPROACH

From a total of 79,057 entries, 995 compounds are semiconductors with negative formation enthalpies; by computing their phonon dispersions, we found 450 of them to be mechanically stable. Thermodynamic stability was then investigated, yielding 75 stable compounds. The lattice thermal conductivity has been computed fully ab-initio, employing novel techniques recently developed in our group (program ShengBTE). Their validation is illustrated in Figure 1a and the values obtained for HH compounds in Figure 1b. The ZT was also estimated ab-initio, from 100 to 1200K in the small grained approximation, which is expected to describe sintered nanograined materials. Machine learning algorithms were implemented to dramatically increase computation speed and compound screening efficiency.

## RESULTS

We find that bulk ordered half-Heusler compounds with κ<3W/(m.K) values are very likely to exist. We show that nanograined HHs compounds are expected to have significantly higher overall ZTs than IV and III-V semiconductors, with many compounds potentially reaching ZT >2 at high temperature. This point is illustrated in figure 2.

## CONCLUSIONS AND PERSPECTIVES

There are many new unexplored half-Heuslers with potentially good thermoelectric properties. Selected candidates are planned to be experimentally tested at LITEN. The results corroborate the competitiveness of machine-learning methods towards accelerated material design.

## PARTNERSHIP


Work in collaboration between with the Center for Materials Genomics of Duke University, led by Prof. S. Curtarolo. Partly supported by project CARNOT SIEVE.



**References**

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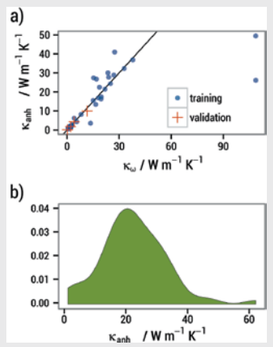


**Fig. 1**
a) Validation of approximated thermal conductivity descriptor versus exact one. b) Distribution of thermal conductivity amongst the half-Heuslers.

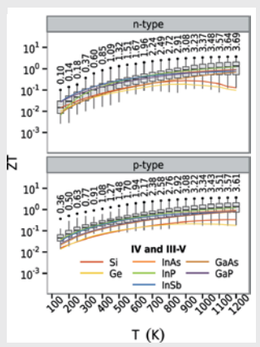


**Fig. 2**
Distribution of nano-grained ZT at different temperatures for the stable half-Heuslers, compared to standard semiconductors.


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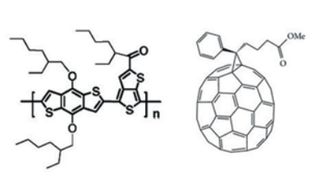
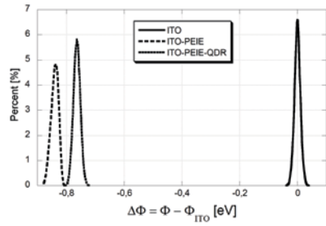
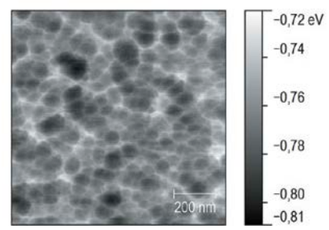
# Work function tuning for high performance solution-processed organic photodetectors with inverted structure





## SUMMARY

**Organic photodetectors with inverted structure are produced by wet process techniques. A very thin interfacing layer of polyethyleneimine leads to a homogenous interface with low work function. The devices exhibit excellent performances, in particular in terms of low dark current density, wide range linearity, high detectivity and remarkable stability in ambient air without encapsulation.**


## CONTEXT

Solution-processed organic electronics offer good opportunity for the manufacture of cost-efficient functional devices. Nevertheless, in the field of organic-based photoactive devices, organic photodetectors (OPDs) have been scarcely studied though they show great potential in various applications. A main goal in the fabrication of such devices is to obtain a good control of interfaces, and in particular for the electrodes.

## APPROACH

The use of a very thin interfacing layer of an organic polymer proved remarkably efficient for achieving homogenous interface with low work function, which leads to very low dark currents (2nA/cm$^2$ at -2V bias) by preventing unwanted charge injection from the cathode.

## RESULTS

We demonstrated that this concept can be efficiently used to produce high performance full solution-processed organic photodetectors. An inverted stack with ethoxylated polyethylenimine (PEIE) and PEDOT/PSS interfacial layers allows fixing respectively the work functions of the cathode and the anode. In particular, we have shown that the work function of the ITO can be lowered by 0.84 ± 0.02 eV very homogeneously. The active layer is a blend of PBDTTT-C and $PC_{70}BM$ (fig 1). Such simple architecture, without any additional blocking layer, gives a particularly low dark current (2 nA/ cm$^2$ at – 2V bias) which is among the lowest reported dark currents for OPDs based on bulk heterojunctions (fig 2). In addition, high detectivity (~$10^{13}$ Jones at 680 nm) and large photocurrent linearity (> 7 decades) were measured. Moreover, no evidence of degradation was observed after storage in ambient air for months.

## CONCLUSIONS AND PERSPECTIVES

Solution-processed OPDs in the inverted stack have been demonstrated with promising optoelectronic performances and environmental stability.

## PARTNERSHIP

ISORG


**References**

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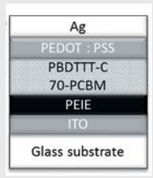


**Fig. 1**
Schematic representation of the photodetector structure

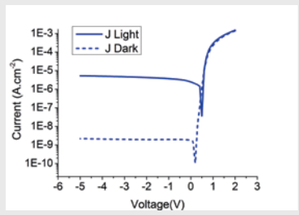


**Fig. 2**
Typical J-V curve of the photodetectors. Measurements were realized at 520 nm with a 25 µW/cm$^2$ power.

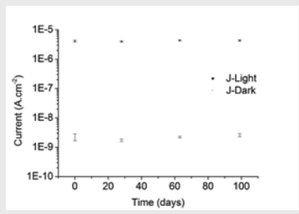


**Fig. 3**
Evolution stability of current densities $J_{Dark}$ and $J_{Light}$ for non-embedded systems during a 100 day period.
Error bars represent the standard deviation measured on 10 systems at VBias= - 2 V.


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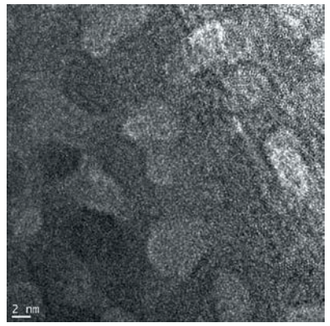
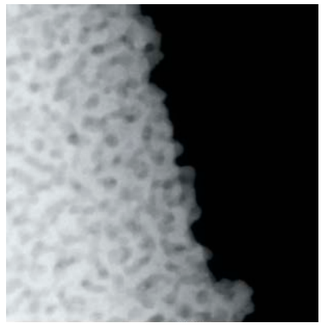
# Low temperature, solution-processed metal oxide thin film transistors




## SUMMARY

**Non-Si-based electronic devices such as inorganic Amorphous Oxide Semiconductors (AOS) are of particular interest for high-performance flexible electronic devices. However their processing route remains expensive. We have developed a low cost processing path and studied the influence of alloying element such on the resulting electrical properties of metal oxide In-Ga-Zn-O (IGZO) semiconductors.**


## CONTEXT

Non-Si-based electronic devices using organic, inorganic, and hybrid materials have been widely reported (K. Nomura *et al,* Nature 2004). Among these materials, inorganic Amorphous Oxide Semiconductors (AOS) are of particular interest (*J. K. Jeong et al, Appl.Phys. Lett. 2007*), and integrating them into active channel layers to produce AOS-based thin-film transistors (AOS-TFTs) is currently being done by Asian manufacturers. They are however processed with conventional vacuum deposition techniques that necessitate high equipment costs, large footprint, and require indirect patterning. Moreover, typical curing temperatures around 450°C are required (*D. H. Lee et al, Adv. Mater., 2007*) preventing any integration in low cost plastic substrate.

## APPROACH

In this work, we investigate an innovative approach based on solution processed metal oxide alloys. Main advantages expected are easier control of stochioemetry, higher electrical performances, compatibility with printing techniques, and consequently low cost.

## RESULTS

Among various attempts to achieve efficient low temperature manufacture and to decrease curing temperature, ultraviolet (UV) photo-annealing was found to be a most promising option for sol-gel metal oxide films due to effective elimination of organic components and acceleration of M-O-M condensation by a combination of thermal annealing and UV irradiation. UV photo-annealed TFT made of In-Zn-O were found to exhibit an enhanced the performance exceeding 3 $cm^2(V.s)^{-1}$ after curing at 325°C as illustrated in Fig. 1. We have studied the effect of In/Zn ratio variations on the electrical properties. Indeed, metal ions of AOSs serve two purposes: In provides high electron mobility due to large atomic radii and to the overlap between adjacent spherical orbitals creating electrical conduction paths. As illustrated in figure 2, excess indium incorporation into In-Ga-Zn-O results in enhancing the field effect mobilities of the TFTs due to the increase in conducting path ways. A field effect mobility of 10 cm2.$(V.s)^{-1}$ has been reached which is higher by an order of magnitude to those of hydrogenated amorphous Si transistor.

## CONCLUSIONS AND PERSPECTIVES

In summary, we have synthesized precursor solutions for deposition of thin In-Ga-Zn-O films into active channel layers of TFTs, with varying indium mole ratios. We have shown that optimized indium content in solution-processed In-Ga-Zn-O TFTs can provide significant improvements in the performance of these transistors. Moreover ultraviolet (UV) photo-annealing was found to allow a significant decrease of the curing temperature of sol-gel based AOSs.

## PARTNERSHIP

IMEP, Merck, Cea DSM

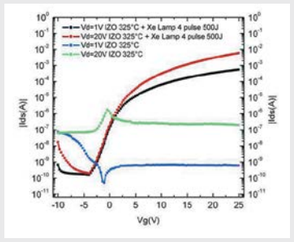



**Fig. 1**
The UV photo-annealed TFT

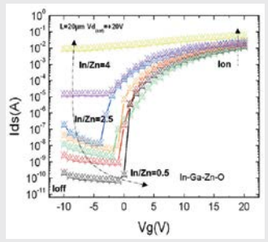



**Fig. 2**
The effects of the indium content on characteristics of IGZO


## TEAM

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# Manufacturing of NdFeB sintered magnets on the new LITEN pilot line



## SUMMARY

**NdFeB sintered magnets have been manufactured by powder metallurgy on the new pilot line developed by LITEN. A maximum energy product $(BH)_{max}$ of 350 kJ/$m^3$ has been produced with 0.5% Dysprosium.**


## CONTEXT

$Nd_2Fe_{14}B$ is the hard magnet type which shows the best compromise between a high remanence Br (1.4 T) and high coercivity $H_c$ (about 1000 kA/m) [1]. For high temperature applications such as hybrid vehicles, expensive Dy has to be added. Studies on microstructure showed strong improvement on Hc without Dy addition [2].

## APPROACH

Strip-casted ribbons with 0.5% wt Dy are decrepitated by hydro-genation at 20°C to produce coarse powder. Hydrogen is then partially desorbed at 550°C under vacuum, and the powder is milled in a semi- industrial jet miller (Hosokawa). In this equipment, a fluidized bed is obtained by introducing a gas flux up to 150 $m^3$/h, and grinding is achieved by the collisions between the particles. An in-line particle sizer is also installed to control the classifier directly. The obtained powder shows a particle size distribution (PSD) centered on 5 µm and a d90/d10 ratio close to 6 (Figure 1). Controlling the grinding energy is a key point to mill without destroying the intergranular Nd-rich phase already present within the ribbons. Powder also needs to be handled in a glove box to avoid oxygen contamination. The jet-milled powder is then pressed under magnetic field (pulses up to 8 T) in order to orientate the c-axis (easy magnetization direction) of each grain in the same direction. A good alignment together with a high density allows to achieve high remanence. Sintering and annealing are finally performed in a metallic furnace (ECM). Green parts have been sintered at 1050°C during 2 hours under secondary vacuum and cooled at more than 3000°C/hour. The final density is above 7.5 g/$cm^3$ and the growth of few abnormal grains has been observed (Figure 2). Annealing is applied to improve the Nd-rich phase distribution around the magnetic particles; it has been performed at 800°C in order to re-melt the Nd-rich phase. The first magnets completely achieved on this new pilot line give a maximum energy product $BH_{max}$ of 350 kJ/$m^3$, Br values around 1.34 T and coercivity $H_c$ up to 1000 kA/m (Figure 3).

## CONCLUSIONS AND PERSPECTIVES

Regarding the difficulty of such a process, remanence and coercivity need to be improved to 1.39 T and 1080 kA/m respectively mainly by reducing oxygen content, particle size distribution ($d_{90}/d_{10}$=5) and a better control of the annealing. Moreover, complex shapes and orientations are studied by Powder Injection Moulding method. This required the mastery of anisotropic sintering.

## PARTNERSHIP

PMB (Alcen) and Vial consulting are our main partners in the development of this pilot line


## FUNDING

This project was partly carried out as part of a collaborative contract with PMB and the French DGA (General Direction of Armament)



## TEAM

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**References**

[1] Sagawa *et al.*, J. Appl. Phys. 55 6 (1984)
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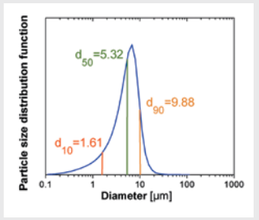


**Fig. 1**
Particle size distribution of NdFeB powders produced by jet mill determined by in-line particle sizer

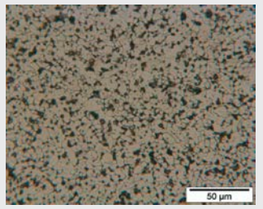


**Fig. 2**
microstructure of sintered magnets after acid etching

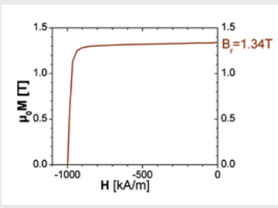


**Fig. 3**
Hysteresis curve of a NdFeB magnet at 20°C

# In situ deformation monitoring as an aid to the determination of the densification law of metallic powders during Hot Isostatic Pressing






## SUMMARY

**Accurate prediction of the shape modification of powder cans during HIP is an issue. The HIP laboratory has been equipped with an in-situ measurement system allowing measuring the real-time deformation.**


## CONTEXT

Powder metallurgy allows achieving complex shaped parts for many applications and industrial sectors. PM technologies are very diverse, but Hot Isostatic Pressing is the key process when large complex parts are required [1]. In HIP, a metallic can is filled with powder, evacuated, sealed and finally compacted under high pressure (typically P=1000 bar) and at high temperature (typically T>1000 °C). A good knowledge of the powder densification behaviour is required to predict, through finite element calculation, the shape of the can after HIP.

## APPROACH

The powder densification behaviour can be evaluated thanks to cans compacted at various duration, T, P conditions. This approach is however incomplete and very time consuming. The other approach developed at LITEN is to monitor the deformation of the cans in situ inside the HIP unit, thanks to high T, high P sensors.

## RESULTS

High temperature capacitive sensors have been chosen because of their small size and the absence of contact with the can. First, coaxial feedthroughs displaying a nylon dielectric membrane have been designed, manufactured and tested for tightness up to 1350 bar. They are inserted in a plug that is used also for thermocouples (Fig. 1). This small plug is in turn inserted in the bottom plug of the HIP unit. Then, two sensors have been integrated inside the HIP unit. A dedicated support plate has been designed to hold these sensors together with the resistor (Fig. 2). Shielded wires have been used to reduce the noise due to resistor electric pulses. The signal of the first one is used to correct the signal of the second one from the voltage variation due to pressure variation. The second one, initially placed very close to the can, measures its move during densification. An example is given in Fig. 3, where it is shown that the powder is densified mainly in the 650-1000°C range.

## CONCLUSIONS AND PERSPECTIVES

These results allow studying in a direct way the behaviour of different powders during different HIP cycles and to provide adequate raw data for shape modelling needed to improve shape prediction. However, in order to improve the accuracy of the measurements, it is planned to add extra sensors and to optimise shielding of the wires.


## PARTNERSHIP

AREVA NP, Aubert & Duval, Erasteel, University of Burgundy.

## FUNDING

This work was carried out as part of the FUI national program ENERPOUDRE. [2]



**References**

[1] PM HIP technology, leaflet from European Powder Metallurgy Association (www.epma.com)

[2] B Picqué *et al.* Hot Isostatic Pressing for the Production of Bimetallic Nozzle for Nuclear application", 11th int. conf. on hot isostatic pressing , Stockholm, 9-13 june 2014


**Fig. 1**
Plug with feedthroughs for capacitive sensors and TCs

**Fig. 2**
HIP resistor and its plugging onto the bottom HIP unit plug

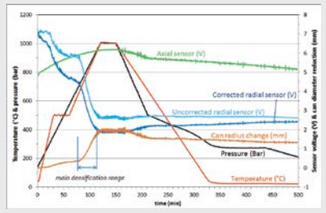


**Fig. 3**
Can radius change during progress of a HIP cycle


## TEAM

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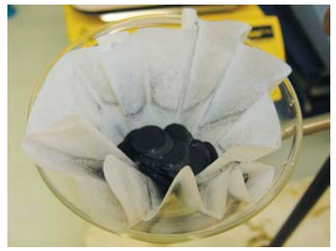
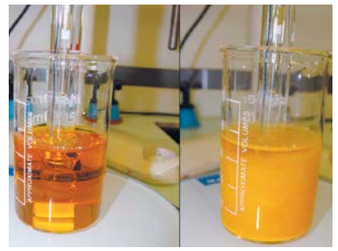
# High efficient recovery of Pt from spent PEM fuel cells by hydrometallurgy


## SUMMARY

**The recovery of platinum in the catalyst layers of PEMFCs (proton exchange membrane fuel cells) is necessary to reduce the cost of this technology. The process developed in this work includes a leaching step from a aqua regia solution; followed by a precipitation step of platinum salt $(NH_4)_2PtCl_6$. This salt can be used either for the synthesis of a new catalyst or for the production of a metal. Considering both steps, the recovery efficiency is higher than 80%, which bring out the potential of this strategy**


## CONTEXT

Nowadays, energy efficiency and renewable energies are central concerns to develop sustainable energy. Among the diversity of technologies, Proton Exchange Membrane Fuel Cells (PEMFCs) represent a promising alternative to fulfill energy requirements in the next decades. To reduce the cost of this technology, there is a strong interest to develop an effective and economically viable recycling process for platinum. The Platinum catalyst represents about 25% of global system cost of PEMFC. This catalyst is immobilised in the MEAs (membrane electrode assembly) on carbone particle and can be recovered from the aged MEA or production scrap. The conventional approach to recover platinum from MEAs includes a pyro/hydrometallurgical step which limits the recovery of other components of the MEA and induces massive production of complex toxic gas (HF for example).

## APPROACH

A new path must be developed based on pure hydrometallurgical treatment to widen the number of recoverable components (membranes, graphite or carbon electrodes), and limit the environmental impact. Platinum leaching has been studied for a long time, *[J. CUI 2008]*, *[P. BLAZY]* and Aqua regia (concentrated mixture in HCl/$HNO_3$ 1/3) is presented as the most efficient reactant. But, the use of an acid concentrated mixture is an economical and industrial issue. The main goal of this work is to define the suitable parameters (time, temperature, ratio S/l,..) to preserve efficiency and reduce the toxicity.

## RESULTS

The results obtain during the project allow to define that above 25gPt.mol$^{-1}$ acid (fig 1) and under 70°C (fig 2) they are a drop of leaching efficiency. The low temperature and low acid quantity necessary to recover Platinum allow the significant reduction of the toxic gas emission with same efficiency of traditional processes. After leaching, platinum is precipitated in $(NH_4)_2PtCl_6$ form by adding ammonium chloride in the solution with 90% of efficiency. All results have been transposed on MEAs material which is shown in (fig 3) with success.

## CONCLUSIONS AND PERSPECTIVES

Considering all the steps of the recycling process, the recovery of platinum in PEMFC has been shown with a basic and efficient process. The next stage will form part of the the scale-up process by recycling a higher quantity of MEAs and use the recovered platinum to make new MEAs.


## FUNDING

This work was partly carried out as part of Energies du futures CARNOT INSTITUTE (RECYPAC).



## TEAM

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**References**

[1] "High efficient recovery of Pt from spent PEM fuel cells by hydrometallurgy" SHECHTMAN INTERNATIONAL SYMPOSIUM, CANCUN, June 29 - July 4, 2014

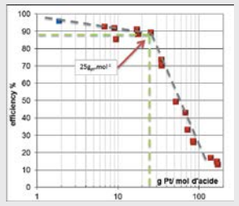




**Fig. 1**
Platinum leaching Efficiency per platinum and acid quantities.

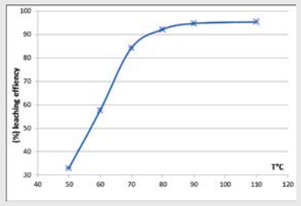



**Fig. 2**
Platinum leaching efficiency to temperature for 25gPt.mol$^{-1}$ acid

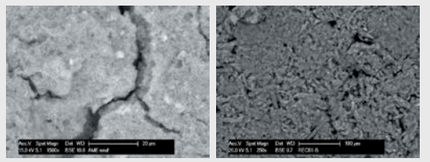
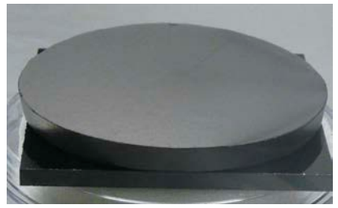
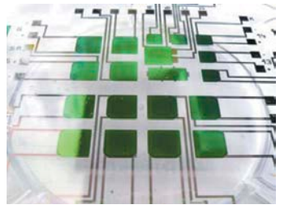
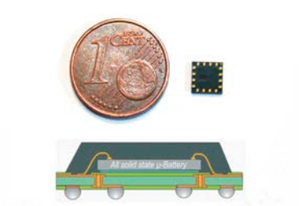


**Fig. 3**
MEA before and after leaching step

# Amorphous lithiated metal (oxy)sulfides electrode materials for lithium-ion microbatteries resistant to the reflow soldering process









## SUMMARY

**New amorphous lithiated titanium oxysulfide thin films as high capacity positive electrodes for 2 V Li-ion microbatteries resistant to the solder reflow were synthesized via a single-step sputtering process, avoiding the use of $H_2S$ and a further Li evaporation step.**


## CONTEXT

All-solid state microbatteries are innovative energy storage solutions for powering microelectronic devices such as ICs, real-time clocks, memories, sensors. Today, most microbatteries available on the market are based on the Li/LiPON/$LiCoO_2$ active core developed at the ORNL [1]. Nevertheless this system is no longer adapted to emerging applications, which now require lower operating voltages (1 to 2 V) and the possibility to connect the microbattery as a conventional electronic component, i.e. using the reflow soldering process.

## APPROACH

$TiO_yS_z$ materials are known to exhibit high volumetric capacities and high cyclability in the 2V/$Li^+$/Li region. Their electrochemical activity involves highly reversible redox processes on both sulfur and titanium [2,3]. In order to manufacture Li-ion cells using an amorphous silicon negative electrode, new lithiated titanium oxysulfide films $Li_xTiO_yS_z$, i.e. in the discharged state, were synthesized via a sputtering process using homemade targets.

## RESULTS

2" Li-Ti-S sputtering targets with different specific compositions were manufactured in order to assess the feasibility of the process and the influence of the film composition on the electrochemical performances.

Dense $Li_xTiO_yS_z$ films with a smooth surface were obtained by radio frequency magnetron sputtering in a pure Ar atmosphere. The characterization of Li/LiPON/$Li_xTiO_yS_z$ cells demonstrated the high capacity (100 µAh·cm$^{-2}$·µm$^{-1}$) and the high cyclability (-0.002%/cycle) of these lithiated electrodes. Higher sulfur content in the positive electrode was found to enhance its specific capacity. Si/LiPON/$Li_xTiO_yS_z$ lithium-ion cells were then fabricated (Fig. 1). Out-of-fabrication cells operating around 2 V (Fig. 2) exhibit also a high cyclability, even at high current rates (Fig. 3). These performances were not notably modified after 3 successive solder-reflow thermal treatments at 260°C.

## CONCLUSIONS AND PERSPECTIVES

The excellent behavior of $Li_xTiO_yS_z$ electrodes in solder-reflowable Li ion cells was demonstrated. The sputtering process using Li-Ti-S targets leads to homogeneous and dense films and especially allows varying and monitoring the film composition more easily. This latter and lithiated amorphous sulfides films are patent pending. The assessment of the process at the industrial scale, i.e. using 6" to 13" targets, is now in progress.

## PARTNERSHIP


ICMCB CNRS (Bordeaux), ST Microelectronics (Tours). This work was achieved as part of the PhD thesis of Vincent Dubois at ICMCB.



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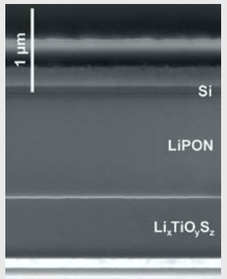


**Fig. 1**
SEM/FIB cross section of a $Li_xTiO_yS_z$/LiPON/Si Li-ion cell

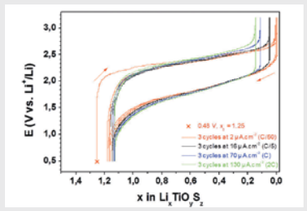


**Fig. 2**
Voltage curves of a $Li_xTiO_yS_z$/LiPON/Si Li-ion cell cycled at various current densities

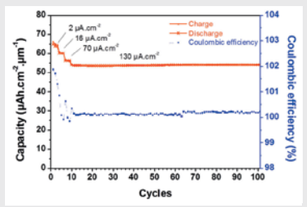


**Fig. 3**
Practical capacity and cycle life of $Li_xTiO_yS_z$ in a Li-ion cell recorded for various current densities


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# Biomasse, Hydrogène et Biogaz
## *Biomass Hydrogen and Biogas*

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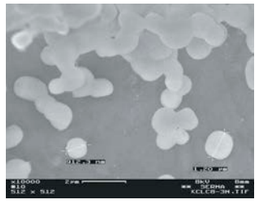
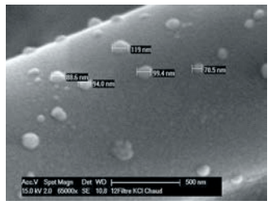
# Biomass ashes behaviour in some high temperature biomass gasification processes




## SUMMARY

**Biomass ashes condensation from high temperature gasifier is investigated in order to improve the management strategy: alkaline chloride deposits could be reduced by external particle addition such as soot, which naturally exists in gasification facilities. Analytical experiments give interesting results for modelling validation.**


## CONTEXT

Biomass ashes contain inorganic species that may form gaseous aerosols or liquid phases depending mainly on the process temperature (between 800 °C up to 1500 °C). Encountered problems are mainly corrosion, pipe fouling and clogging, catalysts deactivation… Present work focusses on the understanding of the inorganic species behaviour that allows a better management of their condensation during gasification in entrained flow reactors (EFR).

## APPROACH

At high temperature (above 1200 °C), condensable inorganic species are chlorides in gasification while sulphates can be found in combustion [1]. Potassium and sodium chlorides were selected to simulate condensation in an analytical experiment [2], under representative cooling conditions (from 1 000 K/s at the reactor output to 300 K/s in the heat exchangers). Main test parameters are salt concentration, the addition of carbon particles (simulating soot for instance) and cooling kinetics. The aerodynamic diameter of the particle distribution is measured by a low pressure electrical impactor (ELPI). Mass concentration is deduced from ionic chromatography analysis after sampling, particle deposits is estimated from a mass balance.

## RESULTS [2,3,4]

Main physical processes that lead to condensation, driven by the ratio of the partial pressure over the saturation pressure for a given species and temperature, were identified during analysis of the experimental results obtained at 1000 K/s cooling rate : homogeneous nucleation takes place from salt vapour when no pre-existing particles are present (small particle diameters are observed, see fig. 1), together with wall deposits (about 60wt%). Injection of carbon particles promotes the heterogeneous nucleation on the pre-existing particles (growing diameter and reduced number of particles) and decreases the wall deposits by about 10wt%. Modelling with the SOPHAEROS* software helps the understanding and quantification of the different mechanisms contributions. Calculation results compare well with the experimental results. The influence of the pre-existing particles is well reproduced, and increase of the external particles addition can be used as a way to decrease the inorganic species wall deposits (fig 2).

## CONCLUSIONS AND PERSPECTIVES

Lot of results were obtained in order to validate the modelling under experimental representative gasification conditions for the first time. Experiments with salt mixtures are in progress and influence of a lower cooling rate (300 K/s) is going to be investigated.
Modelling will be improved and management strategy of the inorganics species will be proposed.

**Please note**

Part of this work is done as part of the PhD thesis of L. Jimenez (in progress).

*: IRSN Software


## TEAM

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## CONTACTS

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**References**

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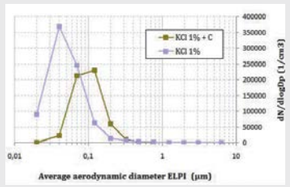


**Fig. 1**
Potassium chloride (KCl) condensation without and with pre-existing carbon particles

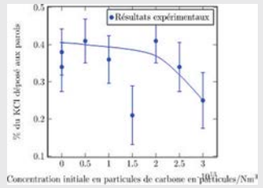


**Fig. 2**
evolution of the wall deposits versus the relative amount of added carbon particles.



# Thermo-chemical conversion of wet biomasses for energy applications



## SUMMARY

**A new family of processes is being developed specifically for the conversion of wet biomasses into biofuels. In subcritical conditions, organic matters like micro-algae, agro-industrial residues can be converted into a green crude. In supercritical conditions, organics are gasified into a producer gas.**


## CONTEXT

Wet biomasses cannot be converted through classical high temperature processes like gasification due to a high energetic cost for water elimination. In this context a new thermochemical family of processes is being developed, making use of the specific properties of water in subcritical or supercritical conditions. In those hydrothermal processes water is a solvent but also a reactant. Those processes are well adapted for resources like algae, agro-industrial residues, or black liquor from the pulp and paper industry.

## APPROACH

Biomass is made of different kinds of natural polymers (lipids, proteins, carbohydrates, lignins). Under subcritical conditions (250-350 °C; 10-20 MPa), hydrolysis reactions will occur and the natural polymers will be deconstructed (Fig. 1). This conversion is called hydrothermal liquefaction. The aim is to produce a green crude for the production of biofuels. Above the critical point, gasification is promoted.

## RESULTS

Hydrothermal liquefaction of Nannochloropsis sp. has been studied in a batch reactor. Nannochloropsis was selected as a valuable algae model by our biologist's partners. Liquefaction experiments were performed between 250 and 350 °C for a pressure between 6 and 12 MPa. Biocrude Higher Heating Values between 20 and 35 MJ/kg were obtained regarding to the temperature and holding time during the experiment. The best carbon conversion yield into biocrude is 68% but a high conversion yield is not associated to the best heating value for the biocrude. In order to classify the experimental conditions in terms of efficiency for energy production we calculate an efficiency indicator as the product of the heating value with the carbon conversion yield. This indicator shows that the best temperature for hydrothermal liquefaction is around 300 °C (fig 2) [1]

## CONCLUSIONS AND PERSPECTIVES

This work is the first step of the development of a process route from micro-algae cultivation to a third generation biodiesel (DIESALG project). The next step will be the optimization of the conversion yield and development of a continuous process. Work is also in progress to develop a liquefaction process for agro-industrial residues (LIQHYD project) as well as a gasification process for black liquor (Enerlig project) [2].


## TEAM

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## PARTNERSHIP

LB3M (CEA DSV), GEPEA, Ircelyon, A3I, CCID

## FUNDING

ANR BIOME 2011 (DIESALG, LIQHYD), Carnot Energie du Futur (ENERLIG)



**References**

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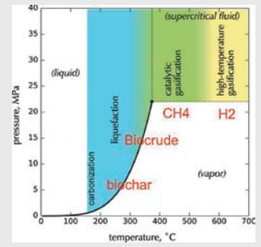



**Fig. 1**
different kind of hydrothermal processes and products according to the water phase diagram

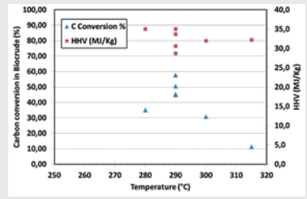
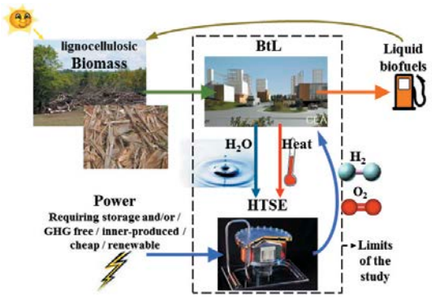



**Fig. 2**
Higher heating Value of biocrude and conversion efficicency of Nannochloropsis under hydrothermal conditions

# $H_2$ production for enhancement of Biomass to Liquid fuel process





## SUMMARY

**Second-generation biofuels are produced by the Biomass to Liquid fuel (BtL) process from lignocellulosic biomass. This feedstock is renewable but limited. An extra hydrogen input to the BtL process doubles the conversion of biogenic carbon. Water electrolysis allows an extensive integration with BtL process, involving oxygen and water, and even free heat with High Temperature Steam Electrolysis (HTSE), in addition to hydrogen.**


## CONTEXT

Second-generation biofuels are produced by the Biomass to Liquid fuel process from lignocellulosic biomass. Hydrogen could be produced from water electrolysis in order to enhance the carbon matter yield. This work addresses the integrated design of the High Temperature Steam Electrolysis (HTSE) and Biomass to Liquid (BtL) hybrid process.

## APPROACH

The comprehensive gate-to-gate analysis includes BtL and hydrogen production on-site operations. Simulations are carried out using commercial process simulation software – ProSimPlus® – to allow physical modelling as well as mass and energy balances; modelling is based on standard elementary and user modules and supported by various previous CEA works.

## RESULTS

Considering productivity, efficiency, cost and environmental issues, five sustainability criteria are chosen for comparison: carbon matter yield; energy efficiency; greenhouse gas emissions; electrolysis water use; levelized biofuels production cost. Simulation results verify that hydrogen input is almost doubling the biogenic carbon conversion into liquid biofuels. They bring out significant secondary energy saving for HTSE compared to the standard process. HTSE coupling allows a sharp increase in productivity (biofuels/biomass) with a limited increase in cost and environmental impacts at almost constant primary efficiency.
Coupling BtL process and hydrogen production by HTSE is therefore promising, offering advanced synergies.

## CONCLUSIONS AND PERSPECTIVES

However, the presented results suffer from major assumptions for estimated or average parameters, such as input biomass or electricity characteristics. For a specific case study, these parameters have to be chosen matching existing situations and sensitivity analysis carried out matching the accuracy of data inputs. Further work would take into account multi-period issues in order to study the suitability of the integrated process with inconstant electrical power.

## PARTNERSHIP

ENSIACET, Université de Toulouse, INPT, CNRS – Laboratoire de Génie Chimique


## FUNDING

This works was carried out as part of a CEA research grant (CFR).


**Please note**

This work is done as part of the PhD thesis of Quentin Bernical.


**References**

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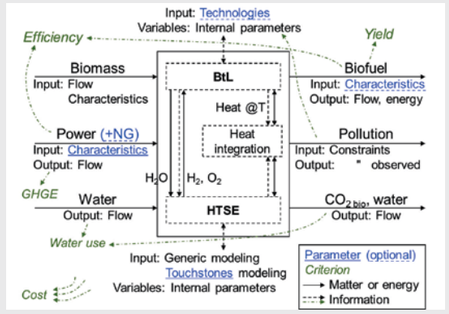


**Fig. 1**
Framework for BtL and HTSE hybrid process evaluation

| | Standard BtL | BtL + HTSE |
|---|---|---|
| Biogenic carbon yield | 33% | 62% |
| Primary Energy efficiency | 42% | 39% |
| GHGE ($g_{eq\ fossil\ CO2}$ / $kWh_{liquid\ biofuels}$) | 14 | 41 |
| Additional water use ($kg$ / $GJ_{liquid\ biofuels}$) | reference basis | + 12 (+ 51 without water reuse) |
| Levelized cost ($€_{2011,\ France}$ / $L_{liquid\ biofuels}$) | 1,4 (capex: 0,98€) | 1,5 (capex: 1,78€) |

**Fig. 2**
Comparison of standard and HTSE hybrid BtL process


## TEAM

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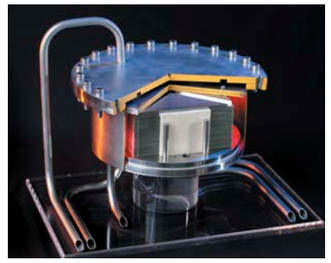
# Reversible operation of a Solid Oxide Electrolyser




## SUMMARY

**Hydrogen is an option for intermittent renewable energy storage. Electrolysers and fuel cells are key technologies for that purpose. Solid Oxide Technology might be particularly suitable, since it can be operated in electrolysis/fuel cell reversible mode. This reversible operation has been validated at small scale, showing that inversion is technically feasible, without any strong accelerated degradation.**


## CONTEXT

Intermittent renewable energies have to be stored to be made available when necessary. Hydrogen is an option particularly suitable for medium to long term storage, while batteries are less efficient due to the self-discharge. In such a case, hydrogen is produced upon electricity excess whereas this hydrogen is consumed to produce electricity when demand exceeds production. In general, beyond the hydrogen tank itself, such storage option requires two devices: an electrolyser on one hand, and a fuel cell on the other hand, both being used only part time, which increases the investment cost.

## APPROACH

Solid Oxide Electrolysis (SOE) has the potential to be a breakthrough technology. It is based on all ceramic cells operated at high temperature (700-800 °C). The same cells are considered for Solid Oxide Fuel Cells (SOFC), producing electricity at the same temperature. Thus, this technology can be operated reversibly, the same device being used either as an electrolyser or as a fuel cell, targeting to decrease the investment cost and to maximise its operation time while improving the efficiency thanks to high temperature. After extensive experimental and modelling activities on either SOE [1-4] or SOFC [5], works have been carried out to evaluate experimentally the ability of the technology to be operated reversibly.

## RESULTS

Experiments have been performed at the single cell level, taking care of the technical feasibility of the inversion (gas inversion and electrical inversion) as well as its effect on the cell durability. 10 inversion cycles have been carried out, shifting from SOE (90%$H_2O$/10%$H_2$) to SOFC (97%$H_2$/3%$H_2O$) through an inversion gas composition of 50%$H_2O$ / 50%$H_2$, each cycle lasting 24 h. Several testing conditions have been applied, with different gas conversion rates. The results show that it is possible to perform this type of inversion with LITEN existing test bench, and that the cell considered for this test is able to be operated in reversible mode without any strong accelerated degradation.

## CONCLUSIONS AND PERSPECTIVES

These results validate the feasibility of the reversible operation. The perspectives consist of a validation of the reversible operation upon different types of cycles and for longer operation as part of collaboration with McPhy Energy, as well as in real stack.

## PARTNERSHIP

Université de Corse, CNRS


## FUNDING

This works was partly carried out within PAGLIA ORBA project funded by EU, French Republic & Territorial Collectivity of Corsica


**Please note**

Part of this work is done in the frame of the PhD thesis of Myriam De Saint Jean.


## TEAM

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**References**

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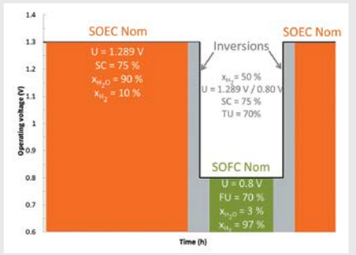



**Fig. 1**
Profile of inversion cycle

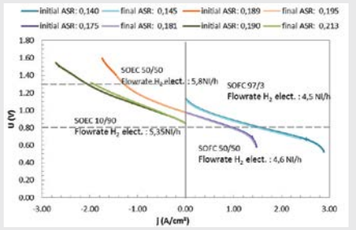
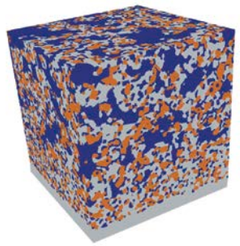
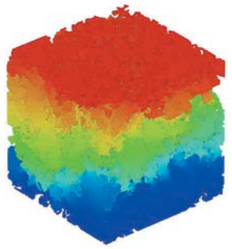
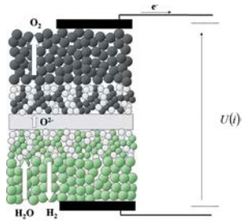



**Fig. 2**
comparison of i-V curves at 800°C before and after the inversion test

# Multi-scale and Multi-physic modeling of Solid Oxide Electrolysis Cell: from electrodes microstructure characterisation to cell perfomance and durability predictions



## SUMMARY

**Efficiency and durability of Solid Oxide Electrolysis Cells (SOECs) are key points for the development of High temperature Steam Electrolysers (HTSE). In this light, it is essential to ensure a better understanding of the basic local phenomena that govern the macroscopic cell behaviour in terms of performance and degradation.**


## CONTEXT

Hydrogen used as an alternative energy carrier has received an increasing interest in recent years. In this context, high temperature steam electrolysis in Solid Oxide Electrolysis Cells (SOECs) appears as a promising technique for massive hydrogen production. However, this technology will be competitive only if the efficiency and durability of SOECs are improved all together. It is therefore necessary to establish a better understanding of the basic relationships that link the electrode microstructure characteristics to the macroscopic cell performances.

## APPROACH

As the global SOECs response is complex and dependant on local electrode properties, a multi-scale and multi-physic model has been developed [1-3]. Key parameters of the model can only be determined via 3D dimensional reconstructions of electrodes. Synchrotron X-ray nano-tomography has been used, taking advantage of the high resolution and large field of view of this technique (line ID 22, ESRF) [4].

## RESULTS

The methodology has been applied to a commercial cell composed of a Lanthanum Strontium Manganite (LSM) anode, Yttria Stabilized Zirconia (YSZ) electrolyte, and Nickel-YSZ cermet cathode. The electrode overpotential has been simulated at the microscopic scale as a function of temperature (Fig. 1). A deconvolution between the thermally activated processes has been proposed. This allows basic degradation mechanisms to be investigated. These results were introduced as inputs in a macroscopic cell model that was experimentally validated. Maps of electrolyser operation have been then computed in terms of cell temperature, hydrogen production rates, etc… (Fig. 2). It has been found the Ni agglomeration in operation explains to a large extent the loss in cell performances.

## CONCLUSIONS AND PERSPECTIVES

A numerical tool has been developed to estimate cell performances and degradation taking into account real cell microstructure. The numerical results will be discussed in order to propose a strategy to increase the cell efficiency and limit the degradation, in terms of cell operating management. Microstructure related properties will also be studied for other materials and conversion systems.

## PARTNERSHIP


ESRF (P. Cloetens and J. Villanova)
CEA-Leti (P. Bleuet)



**References**

[1] J. Laurencin, R. Quey, G. Delette, *et al.*, JPS, 198 (2012) 182.
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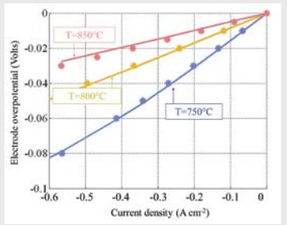


**Fig. 1**
Simulated Ni-YSZ electrode polarisation curves at 750, 800 and 850°C.

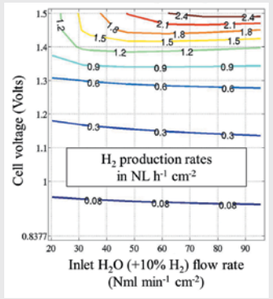


**Fig. 2**
Hydrogen production rates simulated as a function of cell voltage and inlet $H_2O$ (+10%$H_2$) flow rates (T=800 °C)


## TEAM

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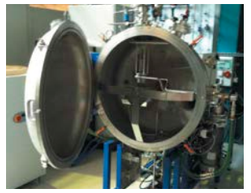
# Development of low cost hydride materials with optimized properties




## SUMMARY

**Hydrogen can be efficiently stored in metallic material absorbing hydrogen namely hydrides. Some of these materials have already been identified as good candidates because absorption and desorption conditions are closed to ambient temperature and pressure; unfortunately they are still too expensive for commercialisation. So the objective of CEA R&D is to lower the hydride production cost according to target markets.**


## CONTEXT

As an energy vector, hydrogen can be used for different applications such as energy management, fuel for backup systems or heavy duty vehicles where it needs to be stored. For the above applications, Solid storage through hydrides is an interesting solution because it offers the key advantage of working at relatively low pressures with high energy density. Some reversible hydride materials for hydrogen storage are already available, but they are still too expensive.

## APPROACH

The objective of CEA R&D is to lower the price of the hydride material using cheaper raw precursor materials, i.e. materials containing more impurities. This approach is done on AB and BCC type hydrides alloys such as TiFe and TiVFe. Process optimisation is also another concern (duration of heat treatment, melting furnace technology…). In order to reach preindustrial scale, a special induction furnace has been designed and installed (see photos in the headline of this page). It allows production of ingots up to 2kg at temperature up to 1900°C.

## RESULTS

A nominal composition of the hydride has been chosen thanks to its good absorption capacity and thermodynamical conditions (Fig. 1). In an "analytical" approach, some elements found as impurities in the raw materials are then added on purpose to the nominal pure material, and their consequences are then analysed in terms of capacity decrease, kinetic influence and activation ability. The material is also analysed in order to understand how the added element interacts with the nominal structure (formation of new phases, substitution of nominal elements, segregation…) (Fig. 2).

## CONCLUSIONS AND PERSPECTIVES

It has been confirmed that some elements coming from usual pollution of raw materials have no effects, others show positive effects like favouring the activation process by creating some phase that takes easily hydrogen, and others such as Al are quite harmful to the material.

## PARTNERSHIP

This work is done with the LCMTR laboratory in Thiais (M. Latroche)

## FUNDING


This work is supported by an industrial company and a Carnot project (RESHYD)


**Please note**

Part of this work is done as part of the PhD thesis of Jean-Benoit Denis.


**References**

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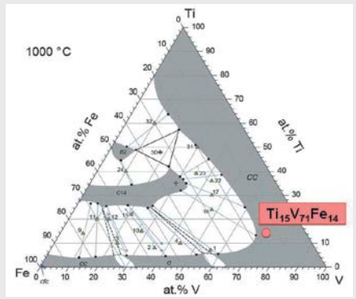


**Fig. 1**
Choice of a hydride nominal BCC composition in the TiVFe system [1]

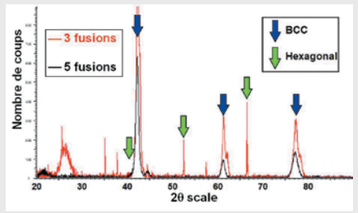


**Fig. 2**
Influence of the number of melting cycles on the phase definition of the formed compound.


## TEAM

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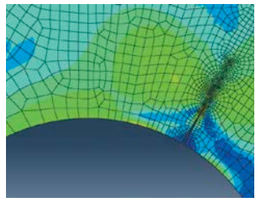
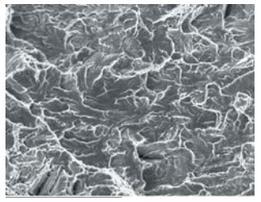
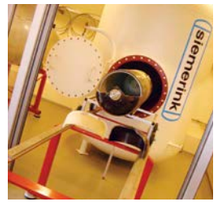
# Material testing and recommendations for hydrogen components under fatigue



## SUMMARY

**The deployment of high pressure hydrogen tanks for energy infrastructure requires adherence to the appropriate international standards and codes. Such standards ensure that these components can be used safely when subjected to hydrogen enhanced fatigue. The European project Mathryce proposed the development of a methodology for material testing and design recommendations dedicated to storage components exposed to hydrogen enhanced fatigue.**


## CONTEXT

High pressure metallic hydrogen tanks (types I to III up to 1000 bar) are subjected to cyclic pressure loadings potentially limiting their lifetime. There are currently no international standards addressing hydrogen enhanced fatigue in the design of such components. It is known worldwide that such standards or codes would greatly facilitate the development of hydrogen infrastructures in the coming years.

## APPROACH

The aim of the project is to define a methodology to design a high pressure tank taking into account hydrogen enhanced fatigue. The assessment will be based on lab-scale tests under hydrogen pressure and full-scale hydraulic tests. The purpose is to avoid full scale tests under hydrogen pressure. Indeed, such tests are very difficult and expensive to carry out. Thus, the approach will rely on a good knowledge of the influence of the relevant parameters, (f, P, DK) on hydrogen embrittlement.

## RESULTS

The material used in this project is a Cr-Mo martensitic steel, currently used for type I cylinder. As shown in Fig. 1, this steel is sensitive to Hydrogen Embrittlement. Under hydrogen, crack initiation appears at a time period close to tank lifetime. On the contrary, crack growth is much more rapid (10 to 100 times higher). A specific device, based on crack gages, has been developed allowing the detection of fatigue crack initiation and the fatigue crack growth measurement under hydrogen pressure (Fig. 2). The choices of the specimen geometry and of the means of detection have been optimised based on mechanical arguments as well as hydrogen testing constraints. Meanwhile, discussions are ongoing with pressure vessels manufacturer and end-users to provide a useful standard.

## CONCLUSIONS AND PERSPECTIVES

The lab-scale results, addressing hydrogen effects, will be used to develop the design methodology. A full scale verification comparing the lifetime of a component under hydraulic and hydrogen pressure cycling loading will be performed.

## PARTNERSHIP

Air Liquide, CIRIMAT, VTT, CSM, CCS, Tenaris, JRC
Current contacts with SNL (USA), Hydrogenius (Japan)


## FUNDING

This works is carried out as part of the European FCH-JU program (MATHRYCE project)


**Please note**

Part of this work is done as part of the PhD thesis of M. Escot.


**References**

[1] Briottet L. *et al.*, Int. J. Hydrogen Energy, 37, 2012
[2] Briottet L. *et al.*, Int. H2 Energy Development forum, Fukuoka, Japan, 2013.
[3] Briottet L. *et al.*, ICHS 2013, Brussels, Belgium, 2013.
www.mathryce.eu

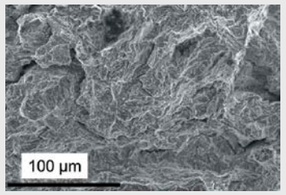




**Fig. 1**
Fractography of a Cr-Mo tensile specimen tested under 300 bar $H_2$

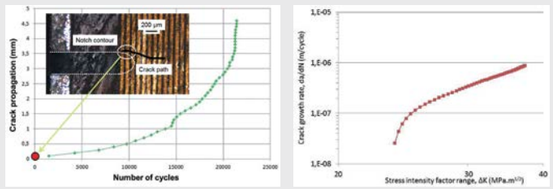



**Fig. 2**
Device development to detect fatigue crack initiation and measure crack growth under hydrogen pressure. Crack gage at a notch tip.


## TEAM

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# Énergie Solaire Photovoltaïque et Thermique
# *Solar Energy: Photovoltaic and Thermal*

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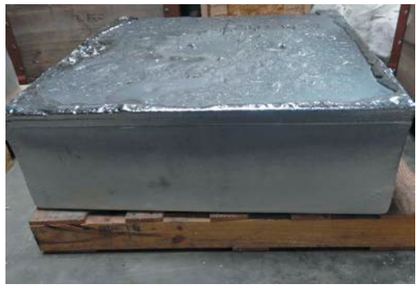
# Purification process by rapid segregation




## SUMMARY

**To reduce silicon purification costs, a new purification process by rapid segregation has been developed within the LMPS laboratory. Different technological systems were tested on a pilot scale directional solidification modified furnace. A successful upgrade to industrial scale showed that it is possible to achieve growth rate objectives whilst keeping good quality material.**


## CONTEXT

Solar Grade Silicon (SoG) can be prepared by different purification steps of metallurgical grade silicon. The last one consists of the metallic impurities segregation by a Directional Solidification (DS) process. The purpose of this work is to develop a new industrial purification process: a specific directional solidification method was developed to ensure effective segregation under rapid solidification conditions.

## APPROACH

The main objective is to ensure a good productivity. For this, the process time which is dependent on the solidification rate and the ingot cooling time must be minimized while keeping good ingot quality. To ensure rapid solidification velocity, it is necessary to increase thermal heat flux extraction under the crucible. For this purpose, LMPS laboratory has developed a new industrial compatible heat exchanger [1] system, based on graphite material. During the silicon melt solidification, metallic impurities segregate towards liquid phase due to thermodynamics conditions. For high solidification rates, impurities accumulate at solid/liquid interface which undergo an instability event for high metallic impurities concentrations. To avoid this, silicon melt must be homogenized by an additional stirring system. This may be achieved by mechanical stirring of the liquid phase [2].

## RESULTS

The thermal heat exchanger and the mechanical stirring system have been first implemented on a DS pilot-scale furnace. Tests with 60 kg of silicon have previously allowed highlighting the effectiveness of the concept. The heat exchanger has the required thermal characteristics allowing an average growth rate of 3 cm/h (twice higher compared to the standard one).


## TEAM

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Different tests without and with stirring have been carried out. The effect of mixing has been demonstrated. The segregation efficiency can be improved by optimizing the mixer geometry. Mechanical stirring increases the material yield of 10 to 20% (fig 1). Technology of the heat exchanger system has been transferred to an industrial scale. It has been implemented on a furnace capacity of 450 to 600 kg (ECM PV600 furnace). Validation tests have allowed verifying the increase of the growth rate from an average speed of 1 cm/h to 2,8 cm/h. These tests have thus demonstrated a productivity gain of about 40% (fig2), consistent with the expectation of the program.

## CONCLUSIONS AND PERSPECTIVES

The next purposes are to realize the technical transfer of the mechanical stirring system and to validate the overall concept at the G5-G6 industrial scale.

## PARTNERSHIP

ECM Technologies


## FUNDING

This works was partly carried out in the frame of an ADEME financed AMI program (PV800Export)



**References**

[1] Patent CEA: FR2968127

[2] Patent CEA: WO2013105060

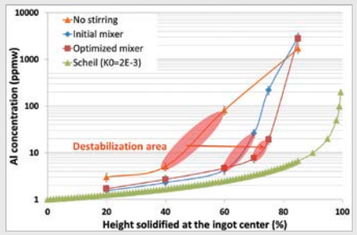




**Fig. 1**
Effect of the stirring on aluminum segregation ($C_0$=500 ppmw): comparison between theory (Scheil law) and experimental results.

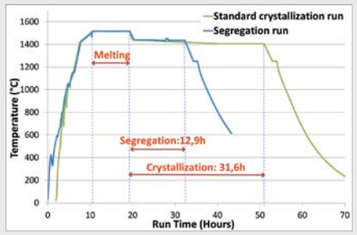
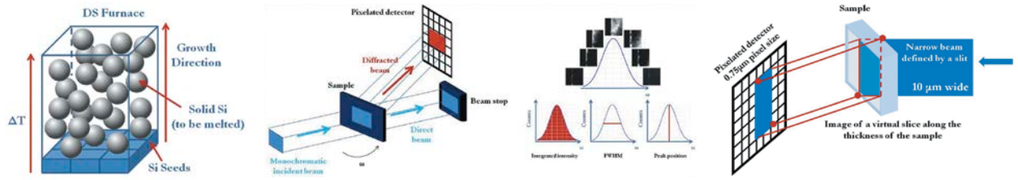



**Fig. 2**
silicon melting/ solidification thermal run time: efficiency of the new heat exchanger system



# Imaging defects during growth of seeded directionally solidified silicon for photovoltaic applications





## SUMMARY

**The generation of structural defects at the junction between the seeds during processing of mono-like photovoltaic silicon by Directional Solidification on a pavement of seeds is being investigated. X ray diffraction Rocking Curve Imaging (RCI) and RCI section topography are applied to analyse the generation mechanisms of dislocation clusters for different seeds misorientations.**


## CONTEXT

Si Ingots of high crystalline quality can be obtained by directional solidification on a pavement of monocrystalline seeds. However, the joints between seeds often lead to the formation of sub-grain boundaries which significantly decrease the efficiency of solar cells. The present work studies the role of these defects in the generation of dislocations and their propagation in mono-like Si ingots grown on seeds with different relative misorientations (<2°).

## APPROACH

The zones containing the sub-grain boundaries were first detected by mapping the charge carrier lifetime with the help of the Microwave PhotoConductivity Decay technique (µW-PCD). The segregation and precipitation of impurities in the area between the two seeds were investigated by micro-Fourier Transform Infrared spectroscopy (µ-FTIR) mapping. And finally, Rocking Curve imaging (RCI) by transmission through wafers with a 200-700 µm thickness range, both in projection and section modes, was used to study the crystalline quality of Si and visualize the defects in the same area.

## RESULTS

Charge carrier lifetime maps reveal that degraded zones can propagate or not from the junction between seeds, as shown in cases “a” and “b” of Fig. 1 for which the seeds misorientation is respectively 0.03° and 1° relative to (004)-plane as measured by RCI peak position. The RCI Full Width at Half Maximum (FWHM) maps in projection (Fig. 2) and in section (Fig. 3) show that in both cases clusters of dislocations propagate along the growth direction. However, while a well defined sub-grain boundary is formed in case “b” with a continuous highly distorted region around it, distortions appear concentrated in separated cones in case “a”, with a local sign reversal in the RCI peak position map (Fig. 3) indicating the presence of groups of dislocations with a strong screw component. In case “b”, the propagation of dislocations from the initial sub-grain boundary toward the seeds is blocked by the presence of an intermediate barrier. SEM and µ-FTIR analyses (Fig. 4) of the zone show the existence of two lines rich in $Si_xO_yN_z$ precipitates induced by the pollution at the initial seed surface.

## CONCLUSIONS AND PERSPECTIVES

As revealed by RCI, the seeds misorientations during mono-like growth of PV silicon plays an important role on the development of electrically active dislocation clusters. Further investigations on the precipitation effect at the seed junction on the dislocation multiplication process are planned.


## TEAM

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## PARTNERSHIP

ESRF


## FUNDING

This work was carried out in the frame of the PVESRF Project of the Carnot Institute on Future Energies.



**References**

[1] M.G. Tsoutsouva *et al,* J Cryst. Growth (2014). doi: 10.1016/jcg

[2] M.G. Tsoutsouva *et al,* Invited talk at ICCGE17 (Warsaw, Aug 2013)

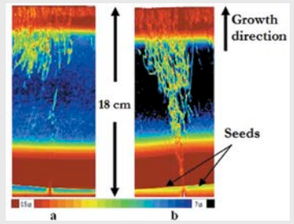




**Fig. 1**
Minority carrier lifetime maps.

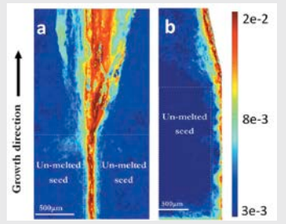



**Fig. 2**
RCI FWHM maps (°).

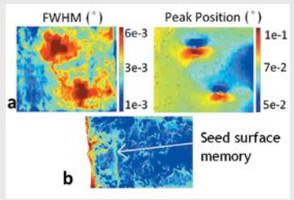



**Fig. 3**
RCI section mode. a) Separated cones with screw component. b) Blocking mechanism of dislocations

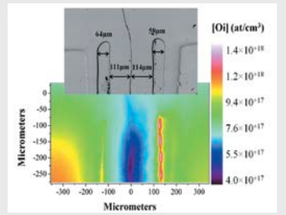
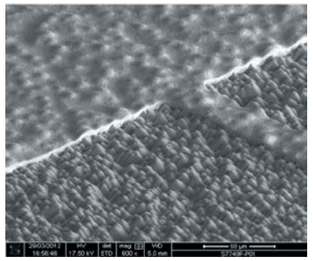



**Fig.4**
SEM image and [$O_i$] µ-FTIR map.

# Turning HIT cells upside down: rear emitter silicon heterojunctions for high efficiency solar cells




## SUMMARY

**In the last two years, HET solar cells (amorphous/crystalline silicon Heterojunction solar cells) have experienced an impressive enhancement of their power conversion efficiency. In particular, an efficient passivation of the crystalline silicon wafers is achieved, while charge carrier transport is optimized. Such improvements could be the result of turning the HET cell structure upside down, meaning placing the emitter in the rear of cells.**


## CONTEXT

Environmental concerns have brought Europe to commit itself towards a change of paradigm regarding energy production. Renewable and delocalized energy sources have been developed, in particular photovoltaic (PV). Nowadays, the PV market has been dominated by standard technologies designed several decades ago. A technological breakthrough bringing to the market more efficient, cost effective devices is necessary to make PV even more competitive with conventional ways to produce electricity. In this context, silicon heterojunction solar [1] cells are promising candidates.

## APPROACH

At the Laboratory for Photovoltaic Components (LCP – now LHET), HET cells have been developed since the creation of the French National Institute for Solar Energy (INES). Recently, we focused our research on the promising concept of rear emitter silicon heterojunction solar cells made of thin amorphous silicon layers deposited on high quality crystalline silicon substrates [2]. Starting from developments made on front emitter structures, we investigated thoroughly several critical points in order to improve cell performance. In particular, lateral transport of electrons was optimized and front recombination losses were minimized.

## RESULTS

The evolution of 100 $cm^2$ cells power conversion efficiency under standard AM1.5 illumination is shown in Fig. 1: a power conversion efficiency of 20.9% using industrial screen printing contacts has been reached. This remarkable achievement has been possible through several advances. For instance, the fill factor of solar cells has increased due to the lateral transport of electron through the n-doped silicon substrate.
Unfortunately, such a cell structure suffers from high recombination losses at the front side because minority carriers have to be extracted at the back. We demonstrated that an optimum exists between parasitic absorption in the front amorphous silicon layer and excellent front interface passivation (see Fig. 2).

## CONCLUSIONS AND PERSPECTIVES

This work allowed us to understand and improve rear emitter HET solar cells. Further developments are being performed to reach 23% power conversion efficiency.

**Please note**

This work will be presented at the forthcoming SiliconPV conference.


## TEAM

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## CONTACTS

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**References**

[1] P-J. Ribeyron *et al.*, Proceedings 23th EU-PVSEC, 2008
[2] R. Varache *et al.*, accepted for publication in Energy Procedia, 2014

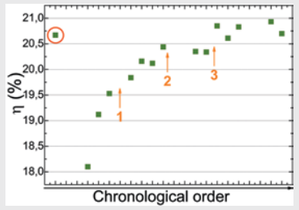




**Fig. 1**
Evolution of cell power conversion efficiency as a function of time. Arrows show major improvements: 1=junction opening; 2= back side optimization; 3= front losses minimization. The encircled point shows the best front emitter cell made in 2013 using screen printing. A 20.9% power conversion efficiency was reached on rear emitter cells.

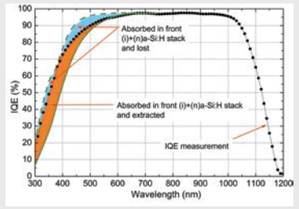
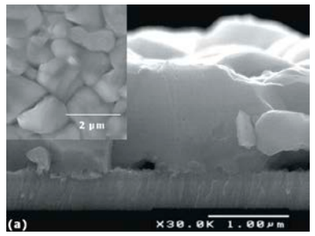
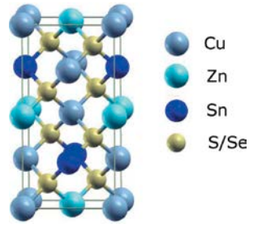


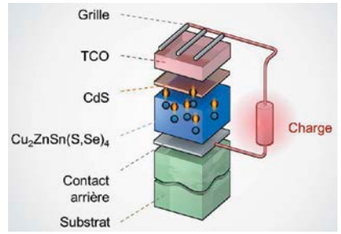

**Fig. 2**
Internal Quantum Efficiency (IQE) measurement and optical simulation, leading to an estimation of front losses due to parasitic absorption of light and recombination of photo-generated carriers. This study lead to the optimization of front amorphous silicon layers thicknesses. Further works are ongoing to make the front amorphous silicon stack more transparent to incoming light.



# $Cu_2ZnSn(S,Se)_4$ thin film solar cells





## SUMMARY

**$Cu_2ZnSn(S,Se)_4$ compound semiconductors are promising candidates for thin film photovoltaic applications. At CEA Liten, the power conversion efficiency of solar cells integrating this new material reaches up to 7% with a conventional buffer layer and almost 6% with a cadmium-free buffer layer. Numerical simulations show that the introduction of a controlled S/(S+Se) ratio gradient in the absorber layer (bandgap engineering) may lead to a significant performance improvement.**


## CONTEXT

The photovoltaic market is currently dominated by crystalline silicon technology. However, thin-film technology offers specific advantages, such as the ability to fabricate light-weight, flexible or even semi-transparent devices. $Cu(In,Ga)Se_2$ (CIGS) and CdTe are the most competitive absorber materials for thin-film solar cells, but the scarcity of In and Te may limit their development at a larger scale. In this context, $Cu_2ZnSn(S,Se)_4$ (CZTS) is a promising thin-film absorber material, since it does not contain any critical element.

## APPROACH

At CEA Liten, we develop CZTS solar cells using a scalable two step process. It consists in the vacuum deposition of precursors on a Mo-coated glass substrate, followed by annealing under Se atmosphere [1]. Solar cells are completed with a buffer layer grown by chemical bath deposition and a ZnO/ZnO:Al (TCO) window layer deposited by sputtering [2].

## RESULTS

Best power conversion efficiencies obtained so far at CEA Liten are 7% with a conventional CdS buffer layer and almost 6% with a Cd-free ZnS-based alternative buffer layer (Fig 1). These results are close to the state of the art for vacuum processes (in 2012, 9.3% have been obtained at Stanford University with a CdS buffer layer). Two trails are under investigation at CEA Liten for improving CZTS solar cell performances:

– A comprehensive study of electrically active defects limiting the efficiency to improve the CZTS material quality itself.
– We have shown using a numerical simulation approach that the efficiency may be increased by up to 15% by bandgap engineering, more specifically by introducing a controlled S/(S+Se) ratio gradient in the absorber (fig. 2) [3]. That could improve the power conversion efficiency independently from the CZTS material quality. This result has been patented [4].

## PERSPECTIVES

Our future work will focus on the fabrication and characterization of highly-efficient CZTS solar cells, notably by using a bandgap engineering approach.

## PARTNERSHIP

CEA-CNRS-UJF group "NanoPhysique et SemiConducteurs", IMEP-LAHC.


## FUNDING

This activity has been partly funded by the SCALENANO European project (grant agreement n° 284486).


**Please note**

Part of this work has been performed as part of the PhD thesis of Giovanni Altamura and Raphaël Fillon.


## TEAM

Louis Grenet, Giovanni Altamura, Raphaël Fillon, Hélène Fournier and Simon Perraud

## CONTACT

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**References**

[1] G. Altamura & al., Journal of Alloys and Compounds. 588C (2013) 310-315.
[2] L. Grenet & al., Solar Energy Materials and Solar Cells. 101 (2012) 11-14.
[3] G. Altamura & al., submitted.
[4] L. Grenet & al., Brevet n°1257749, 10/08/2012.

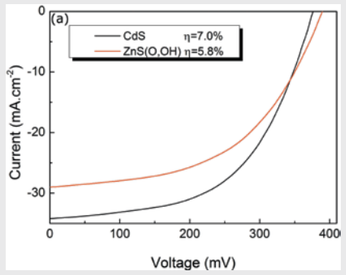




**Fig. 1**
Current-voltage characteristics of the best CZTS solar cells demonstrated so far at CEA Liten (with CdS and ZnS-based buffer layers).

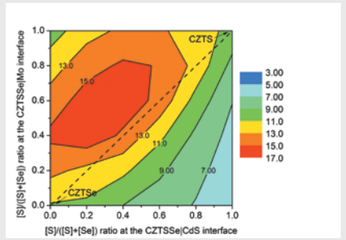
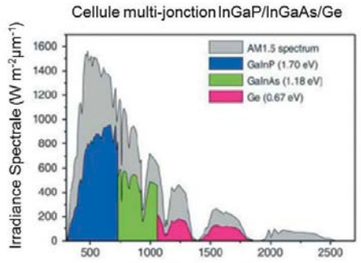
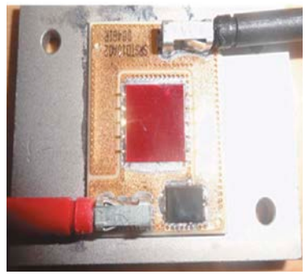



**Fig. 2**
Simulated power conversion efficiencies of a Mo/CZTS/CdS/TCO solar cell as function of S/(S+Se) ratio gradient in the absorber layer.

# Towards comprehension of ageing mechanisms and degradation processes in CPV receivers




## SUMMARY

**A thesis [1] has been conducted between 2011 and 2013 at INES to understand the degradation mechanisms of CPV cell assemblies.**


## CONTEXT

Concentrating Photovoltaic (CPV) is based on the concentration of solar rays on very-high efficiency solar cells. Multi-junction architectures used in CPV systems achieve efficiency up to 44% under concentration. This has created great interest for this technology over the past decade. Nevertheless, CPV reliability has still to be demonstrated. This project is an effective contribution to this goal.

## APPROACH

CPV assemblies – or receivers – are defined by the electrical, mechanical and thermal cohesion of a multi-junction solar cell on an appropriate substrate. The complexity of multi-junction architecture does not allow their characterization with existing PV tools. Therefore, a complete infrastructure for the characterization of such devices has been first developed. Then accelerated ageing tests and analysis methods to study the degradation process of these assemblies have been designed and validated.

## RESULTS

A new method for the characterization of die-attached CPV cell assembly has been proven successful. It is called EEL for Enhanced ElectroLuminescence [2]. This method is cost effective and really fast and has therefore been patented. The performance characterization of CPV cell assembly under illumination has been performed in close collaboration with the Instituto de Energìa Solar (IES) in Madrid, Spain. Thanks to this collaboration, two types of CPV cell assemblies have been studied. One based on the Direct Bonded Copper (DBC) substrate, corresponding to the state-of-the-art and most used type of substrate in CPV industry. The other is a completely new type of substrate, inspired by the Insulated Metal Substrate (IMS). This new IMS based CPV cell assembly has been developed by the CEA and its industrial partners. The reliability study of these CPV cell assemblies (DBC and IMS) has been conducted through accelerated ageing tests. It has been shown that none of the DBC or IMS cell assembly present infant mortality or failure upon ageing.

## CONCLUSIONS AND PERSPECTIVES

This work has launched the CPV activity at INES. The results on receivers now need to be confirmed on complete CPV-modules and systems.

## PARTNERSHIP

Heliotrop, IES, Eolane, GMD, Solutest.


## FUNDING

This work was partly carried out as part of a national CIR program held by Heliotrop Company.


**Please note**

This work was done as part of the PhD Thesis of Loïc Mabille. The results were presented at the conferences CPV8 and CPV9.


**References**

[1] "Toward comprehension of ageing mechanisms and degradation processes of CPV cell assembly", Loïc Mabille , PhD thesis, submitted.

[2] "CPV solar receiver ageing tests: The enhanced electroluminescence Method". Loïc Mabille *et al*. In CPV9 Conference, p.226 (2013) .

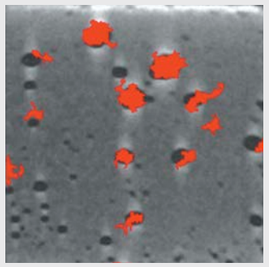



**Fig. 1**
example of void cartography obtained with X-Ray tomography (background) and voids detected by EEL (red – patent pending).

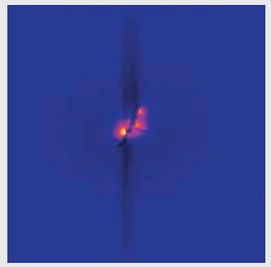


**Fig. 2**
example of a localized crack detected in a CPV-cell by electroluminescence.


## TEAM

Loïc Mabille, T. Baffie, A. Pereira, M. Mariotto, S. Colasson, Ch. Mangeant and LITEN labs

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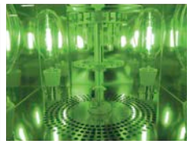
# Towards the definition of accelerated ageing test of solar mirors for concentrated solar power (CSP)




## SUMMARY

**The durability of solar mirrors for concentrated solar power is a key point for this technology. Under operation, the mirrors are submitted to arid climate with extreme temperature, humidity and solar irradiation. Their operational specifications include a lifespan of at least 25 years. Climatic tests under controlled environment are used to study the degradation mechanisms of the mirrors. Results from accelerated ageing with temperature, humidity and irradiation in cycling conditions reproduce well the on-site degradations and open the door for an extended understanding of the involved mechanisms.**


## CONTEXT

By means of large mirrors, CSP (Concentrated Solar Power) technologies concentrate the solar energy on an absorber where it is collected as thermal energy. The decrease of the kWh cost and the insurance of a minimum 25 year lifetime are the key points to make these technologies cost competitive and ensure their large deployment. The durability of the mirrors is a key point for this technology [1,2]. Nowadays, the majority of these technologies use glass mirrors. In operational conditions, the mirrors are submitted to arid climate where temperature, humidity and solar irradiation are extreme.

## APPROACH

Accelerated climatic tests in controlled environment are used to reproduce the mirror degradations observed on site.

## RESULTS

On site, the loss of reflectivity of the mirrors is due to the corrosion of the reflective layer under humidity. This corrosion started from the edge of the mirrors through the degradation of the protective paint layer on the back side (see Fig. 1). The protocol defined for the accelerated ageing at our lab has shown that the degradation of the paint is due to the combination of the sun irradiation, temperature and humidity conditions as for on-site operation. Selecting only one of the environmental conditions is not sufficient to reproduce the mirrors degradation under accelerated tests. These tests combine elevated temperature, humidity and irradiation in cycling conditions. After only 450h, the mirror degradation starts with the same mechanisms as on-site (see Fig 2) showing cracks in the paint layer and corrosion of the silver one.

## CONCLUSIONS AND PERSPECTIVES

By using simultaneously temp-erature, irradiation and rain in test chamber in cycling conditions, the on-site degradation mechanisms of solar glass mirrors has been reproduced. The next step is to apply these tests on different types of solar mirror technologies and determine the factor of acceleration through the correlation between outdoor and indoor ageing studies.

**Please note**

Part of this work is done as part of the Post Doctoral work of R. Girard.


**References**

[1] C. Delord *et al,* Characterizations of the durability of glass mirrors for concentrating solar power, Solar PACES conference, 2012

[2] O. Raccurt *et al,* Correlation between solar mirror degradation and colorimetric measurement of protective back layer, solar PACES conference, 2013

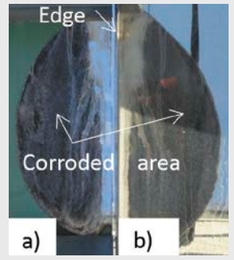




**Fig. 1**
Photograph of a corroded mirror on site a) back side, b) front side

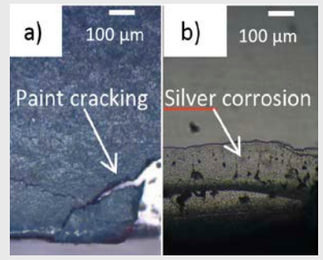



**Fig. 2**
Optical microscopic photograph of accelerated aged mirror (after 450h in Suntest with rain cycling condition) showing (a) cracks in the paint layer and (b) corrosion of silver layer


## TEAM

O. Raccurt, C. Delord, R. Girard, A. Disdier, R. Couturier, C. Bouquet

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# Batteries et Piles à combustible pour la Mobilité
*Batteries and fuel cells for mobility*

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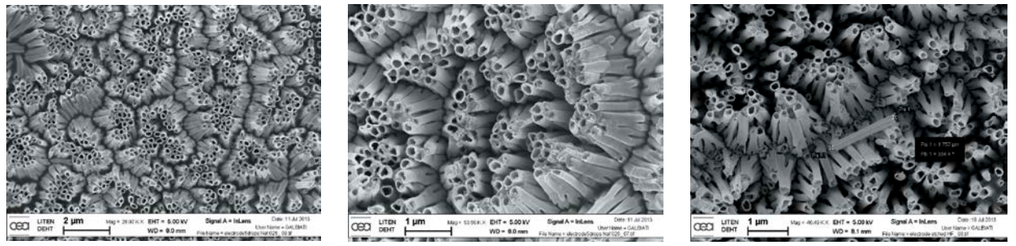
# Arrays of Pt Nanotubes as new effective and sustainable Fuel Cell electrode architecture




## SUMMARY

**A new electrode architecture based on an array of self-standing Pt nanotubes (Pt-NTs) has been developed in order to increase the performance and the durability of Proton Exchange Membrane Fuel Cells (PEMFC). The Pt-NTs electrode is fabricated by Atomic Layer Deposition (ALD) of a Pt layer onto sacrificial templates of porous Anodic Aluminum Oxide (AAO). Electrochemical characterizations in half-cell and preliminary fuel cell tests in real operating conditions revealed the great potential of this new architecture.**


## CONTEXT

One of the main limitations of PEMFC comes from the cathode material. This electrode impacts on the PEMFC in terms of cost, performance or durability. These issues can only be overcome thanks to a breakthrough in its nanostructure. Compared to the current electrodes, made of Pt nanoparticules, an aligned array of Pt nanotubes (Pt-NTs) does not require porous carbon support. This feature should lead to higher stability, larger specific activity and lower mass transport losses and, thus, to a drastic improvement of the efficiency and the durability of a PEMFC.

## APPROACH

Pt-NTs are produced by deposition of a controlled thin layer (10-20 nm) of Pt by Atomic Layer Deposition (ALD) onto a sacrificial template of porous Anodic Aluminum Oxide (AAO). The Pt coated AAO template is stuck onto a Nafion® membrane and alumina is dissolved. The Pt-NTs array is finally covered with a thin Nafion® layer (~20 nm) to increase its proton conductivity (Fig.1). The resulting Pt-NTs (length: 2 µm, $Ø_{in}$:140 nm, $Ø_{out}$:180 nm) are oriented and have dense walls (Fig.s on top of page).

## RESULTS

The ex-situ electrochemical characterizations in half-cell (Fig.2) show that Pt-NTs exhibit a higher gas accessibility and surface activity towards the oxygen reduction reaction: 37 µA/$cm^2_{Pt}$ vs 28 µA/$cm^2_{Pt}$ for conventional carbon supported electrode (Pt/C) [1]. This new architecture has been tested for the first time in real operating conditions. In preliminary tests, the nanotubes array electrode gives a satisfactory response under air at both 50% RH and 100% RH (Fig.3).

## CONCLUSIONS AND PERSPECTIVES

The preliminary results demonstrate the great potential of this new architecture based on Pt nanotubes array. Further improvement of the geometry is needed, namely length, diameter and density of the tubes. New Pt-NTs have been produced by metal evaporation using a lower quantity of Pt, showing good catalytic properties. The use of Pt alloys and core shell structures is foreseen in order to decrease the Pt loading.


## FUNDING

The CEA transversal program on New Technology for Energy and the scientific direction of CEA-Grenoble are acknowledged for funding as part of the NULNE-LEFIS project.



## TEAM

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**References**

[1] S. Galbiati, A.Morin, N.Pauc. Electrochimica Acta 125(2014) 107-116.

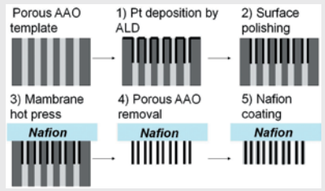




**Fig. 1**
Stepwise scheme of the Pt-NTs productive process.

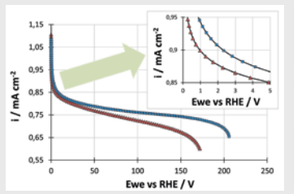



**Fig. 2**
Current-voltage trend under oxygen for Pt-NTs (red) and Pt/C (blue) measured in half-cell setup at room temperature.

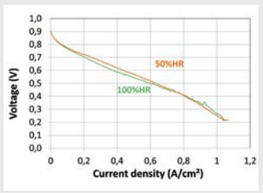
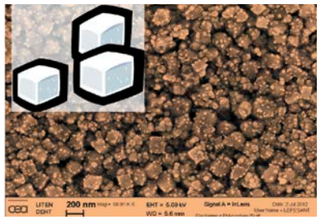
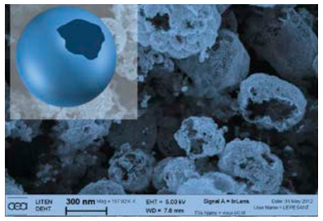
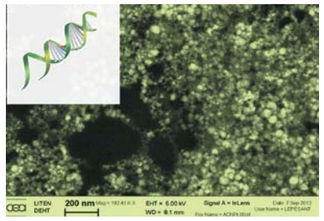



**Fig. 3**
Polarization curve measured during the fuel cell test (17 $cm^2$) of the Pt-NTs under $H_2$ and Air RH=50% (orange) and RH=100% (green), $T_{cell}$=80°C.

# Designing nanotructured platinum or platinum alloy – based catalysts for PEM fuel cell application: control of shape, nanostructure and electrocatalytic property





## SUMMARY

**Advanced nanostructured materials were synthesized and evaluated as electrocatalysts for low-temperature fuel cells. Influence of different morphologies and nanoscale structures of platinum and its alloy particles was studied. Performances and ageing were evaluated and compared to usual catalyst materials at different scales: from laboratory electrochemical setup to real fuel cell operation.**


## CONTEXT

Lowering catalyst costs is one of the essential steps towards making PEM Fuel Cell technology economically viable. Performance of the usual catalysts, most often made of black carbon supported platinum based nanoparticles is limited by their specific surface area and activity. Morphology control of catalysts at nanoscale could lead to an increase of the electrochemically active surface area. A significant reduction of precious metal loading required for optimal operation of PEM fuel cells is possible.

## APPROACH

The use well-controlled morphology of nanostructures [1,2] or templated Pt-based nanoparticles such as "core-shell" or hollow nanoparticles [3], represent some of the advanced routes that were assayed to structure catalysts at the nanoscale. The study of these nanostructured materials would enable a better understanding of the influence of the nanoparticles morphology on the electrocatalytic properties. A further reduction of Pt loading can be expected by partial substitution of platinum by 3d and 4d block non-noble metals.

## RESULTS

A number of different structures such as nanocubes, hollow spheres and DNA – template Pt nanostructures were synthesized and their performances were compared towards the reduction of oxygen reaction. Electrochemical tests were conducted on rotating electrode, half-cell setup and Scanning ElectroChemical Microscopy (SECM). The most promising catalysts were prepared, scaling up the synthesis method from mg to g level. Catalyst powders were then used to prepare full MEAs (membrane – electrode Assembly) to evaluate and compare their performances and durability in real fuel cell operation.

## CONCLUSIONS AND PERSPECTIVES

Very promising results were obtained, both at laboratory scale (three electrodes electrochemical cell) and real PEMFC operation. However, further improvement should still have to be made, particularly on the catalyst support materials, replacing the black carbon powder used as support by a more stable material (conductive metal oxide, graphene…).


## FUNDING

This works was partly financed by DGA (French Defence)


**Please note**

This work is done as part of the PhD thesis of Mathieu Lepesant (09/2011 → 09/2014)


**References**

[1] F. Lazar *et al*. ELECTROCHIMICA ACTA 2012,Vol. 78,98-108
[2] Patents: EP2504467, US2012318675
[3] L. Dubau *et al*. ELECTROCHIMICA ACTA 2011 Vol.: 56 Issue: 28 10658-10667.

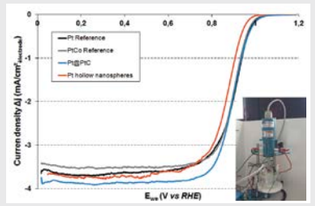




**Fig. 1**
comparison of performance toward $O_2$ reduction of different catalysts at laboratory scale setup (reference materials, Pt hollow spheres and core-shell catalysts). Best performances are obtained on core-shell material.

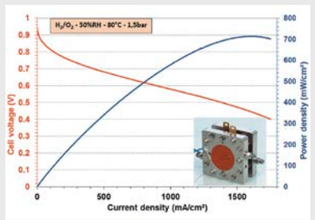



**Fig. 2**
Example of polarization curve obtained in PEM fuel cell real operation (80°C and $H_2$/Air) using advanced nanostructured core-shell bimetallic catalyst Pt@PtCo synthesized at gram scale. Red curve: voltage vs. current density; blue curve: power density vs. current density.


## TEAM

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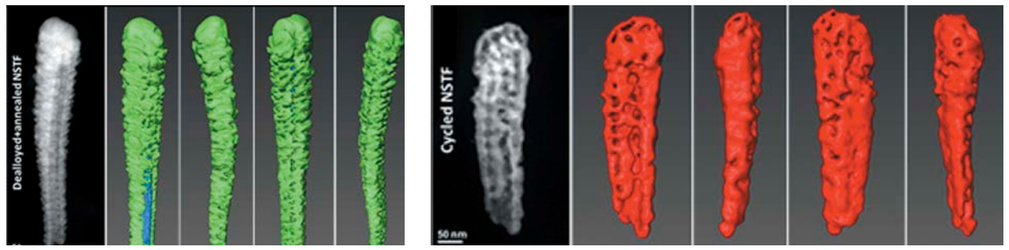
# 3D morphology analysis of highly active $Pt_3Ni_7$ nanostructured thin film catalysts using electron tomography in collaboration with the DOE-Oak Ridge National Laboratory





## SUMMARY

**Through collaboration with Oak Ridge National Laboratory, the 3D structure of $Pt_3Ni_7$ Nanostructured Thin Films was reconstructed using electron tomography, an advanced transmission electron microscopy technique developed at Minatec Nano-Characterization Platform (PFNC). This study reveals the catalyst microstructure evolution after an ageing test under cycling conditions.**


## CONTEXT

$Pt_3Ni_7$ Nanostructured Thin Films (NSTF) are under development by 3M Company as part of a DOE-funded fuel cell project entitled "High Performance, Durable, Low Cost Membrane Electrode Assemblies for Transportation Applications." NSTF are a novel extended surface electrode structure having significant advantages in oxygen reduction reaction activity and stability [1]. They are made from an array of organic support whiskers that is magnetron sputter-coated with Pt alloys. Still under development, $Pt_3Ni_7$ alloy catalysts reveal an unusually sharply peaked gain in activity [2]. The Oak Ridge National Laboratory (ORNL) that performs detailed chemical and microstructural analyses of these NSTF wanted to have a 3D visualization of their structure. Through collaboration with LITEN, 3D reconstruction of NSTF structures were obtained using electron tomography, an advanced transmission electron microscopy (TEM) technique developed at the Minatec PFNC.

## RESULTS

Two whiskers were analyzed: the first one was taken from a fresh electrode and the second one was taken from a membrane electrode assembly aged under potential cycling conditions. The 3D reconstructed structure of the fresh whisker (Fig. 1) reveals the lath shape of the alloy grains deposited on the organic whisker and the lack of metal coverage near the bottom region. The reconstruction of the cycled whisker (Fig. 2) shows that due to the Ni dissolution during the ageing test a network of pores appears within the whisker structure.

## CONCLUSIONS AND PERSPECTIVES

These results will be discussed with regards to the catalyst electrochemical performances [3].


## PARTNERSHIP

PFNC, INAC, ORNL.


**Please note**

This work was performed in collaboration with M. Lopez-Haro (INAC), expert in electron tomography and D. Cullen (ORNL) who spent 4 weeks at the PFNC.


**References**

[1] Debe M. K., Nature, (2012) 486, , 43-51
[2] Debe, M. K. *et al*.. J. Electrochem. Soc., (2011) 158, B910–B918.
[3] Cullen D., paper in progress


**Fig. 1**
3D reconstructed structure of the fresh $Pt_3Ni_7$ NSTF obtained using electron tomography

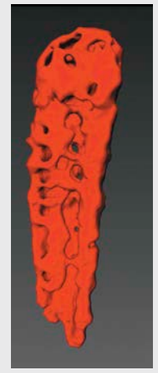


**Fig. 2**
3D reconstructed structure of cycled $Pt_3Ni_7$ NSTF obtained using electron tomography


## TEAM

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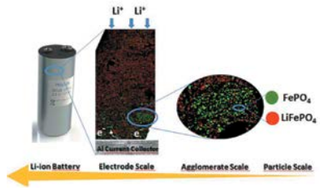
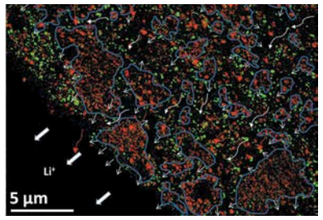
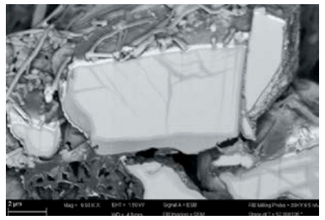
# Electron microscopy study of the lithiation and degradation mechanisms in silicon and $LiFePO_4$ battery materials.




## SUMMARY

**The lithiation mechanisms in silicon (negative) and $LiFePO_4$ (positive) based electrodes have been studied by various electron microscopy (TEM & FIB) techniques, from nanometer to few hundred micrometer scale. For the first time different scale heterogeneities have been evidenced and correlated to the battery degradation.**


## CONTEXT

In order to improve the battery capacity and reduce degradation, a better understanding of the lithiation mechanisms is required. Two promising materials have been studied: Si and $LiFePO_4$.

## APPROACH

For $LiFePO_4$ based electrodes, new automated diffraction techniques such as precession electron diffraction (PED) and Electron Forward Scatter Diffraction (EFSD) were improved to obtain $LiFePO_4$ / $FePO_4$ phase map at nanometer scale. PED is a TEM technique with unrivalled spatial resolution (~2 nm). EFSD is a SEM technique that allows phase mapping on very large field of view (~0.5 mm) with very good spatial resolution (~10 nm). For Si electrodes, since most of the $Li_xSi$ phases are amorphous, plasmon energy loss spectroscopy in scanning transmission electron microscopy (EELS-STEM) was used. Since the $Li_xSi$ phases are very sensitive to air and electron beam, a new methodology of specimen preparation and transfer has been developed. Large scale observations of battery degradation were performed by Focus Ion Beam (FIB).

## RESULTS

In $LiFePO_4$ based electrode, the PED maps confirm the domino-cascade model [1,2]. The EFSD phase maps prove that the lithiation starts from the particles at the surface in direct contact with the electrolyte and propagates "stratum by stratum" (Fig. 1) [2].

In the Si electrodes, the STEM-EELS phase maps (Si, $Li_xSi$ and SEI) clearly show a core-shell lithiation mechanism of the Si nano-particles (Fig. 2) [3]. This result was confirmed on Si micro-particles by Nano-Auger [4]. A size effect of the particles on the lithiation capacity was evidenced (the smaller the particle, the lower x in $Li_xSi$). FIB imaging revealed that after cycling, large Si particles are (de)lithiated along structural defects and that the electrode porosities are closed by the SEI formation [3].

## CONCLUSIONS AND PERSPECTIVES

These results bring a new understanding of the lithiation mechanisms and open the way to material/processing improvements.

## PARTNERSHIP

This work results from collaboration between the different CEA institutes LITEN, LETI and INAC in the Nanocharacterization Center at Minatec. INSA Lyon is also thanked.


## FUNDING

This works was partly carried out as part of national projects Carnot VEHYLOCO and ANR AMOS.


**Please note**

This work was awarded at the conference of GFECI (2013).


**References**

[1] G. Brunetti *et al. Chem. Mater.* 2011, 23, 4515-24.
[2] D. Robert *et al. ACS Nano* 2013, 23, 10887-94.
[3] D. Robert, *thèse CEA*, 2013. http://hal.archives-ouvertes.fr
[4] E. Radvanyi, *et al. J. Mater.Chem.* 2013, 1, 4956–65.

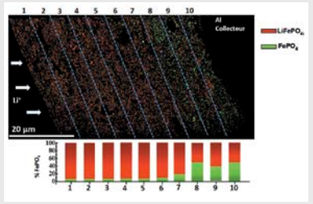




**Fig. 1**
$LiFePO_4$/$FePO_4$ phase maps obtained by EFSD in a fully discharged (lithiated) thick electrode after 45 cycles.

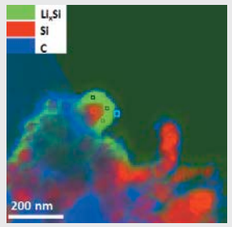



**Fig. 2**
Si and $Li_xSi$ phase map obtained by STEM-EELS in a Si electrode stopped at 40% lithiation. Notice the core-shell structure of the particles.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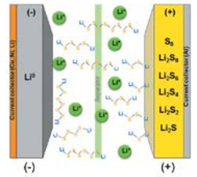
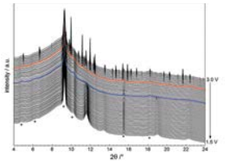
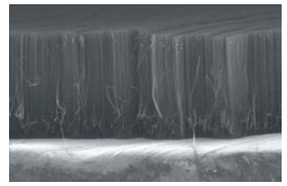
# Development of next generation lithium metal rechargeable batteries: the Li/S technology





## SUMMARY

**The combination of different analysis techniques, such as UV spectroscopy, in situ and operando X-ray diffraction and chromatography, has allowed us to take a step forward regarding the understanding of Li/S battery technology, its discharge process and failure mechanisms. This improved understanding opens up new perspectives for further improvements of the Li/S cell, as well as for other lithium metal battery technologies such as Li-air or Li-polymer.**


## CONTEXT

The development of rechargeable batteries has received increasing attention due to the need of storage systems for portable devices and alternative energy sources. Li-ion batteries are a popular electrochemical storage systems due to their high energy density, high operating voltage and low self-discharge. Li-ion batteries are currently under development at CEA-LITEN, aiming to improve their practical energy density, as well as their cyclability and safety.

With a view to further improve the performances of lithium batteries, CEA-LITEN also develops alternative technologies, such as lithium/sulfur (Li/S) or Li-air batteries. Based on the use of a lithium metal negative electrode, these next generation energy storage systems are indeed promising in terms of gravimetric energy density. In particular, the Li/S system has attracted the attention of electrochemistry community for many years, due to its low cost, non-toxicity, abundance and high theoretical capacity of elemental sulfur active material. However despite three decades of research, the discharge mechanism of the Li/S cell is still controversial as well as its failure mechanisms. In addition practical performances are still below expectations, and some major breakthroughs are still needed for this technology.

## RESULTS

At CEA-LITEN, the combination of different analysis techniques (UV spectroscopy, chromatography, in situ and operando X-ray diffraction) has allowed us to improve our understanding of Li/S systems. [1-2]. The appearance/disappearance of solid $S_8$/$Li_2S$ phases was correlated to the state of charge, and a new crystalline form of sulfur (β-$S_8$) was proven for the first time (fig 1). Then, a discharge mechanism and a degradation model could be proposed. This work enables the improvement of the performances of Li/S cells, through the development of 3D current collectors for $S_8$ positive electrode and new electrolyte compositions [3-4]. For example, vertically-aligned carbon nanotubes grown on aluminium foil and high solvating electrolyte solvents such as PEGDME, allow the progression towards high performances semi-liquid Li/S cells (fig 2).

## CONCLUSIONS AND PERSPECTIVES

The understanding of Li/S system opens up new perspectives for the improvement of this technology, as well as for other Li metal batteries such as Li-air or Li-polymer [5].


## PARTNERSHIP AND FUNDING

CNRS (LEPMI), SOLEIL, ESRF

This work was partly carried out thanks to Institut Carnot "Energies du futur" (SOLIS) and DGA (Sylwia Walùs PhD thesis) funding.



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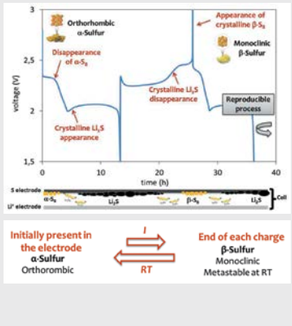


**Fig. 1**
Evolution of sulfur active material structure over cycling, investigated by means of in situ and operando X-ray diffraction.

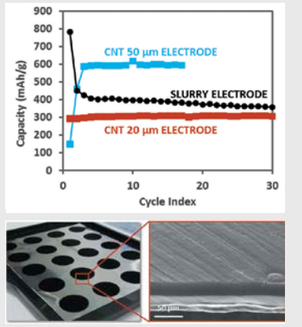


**Fig. 2**
Electrochemical performances of vertically-aligned carbon nanotubes (CNT) substrates as positive electrodes for Li/S batteries.


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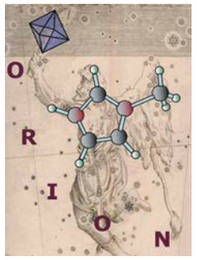
# Ionic liquid-based electrolytes for safer batteries







## SUMMARY

**The use of flammable electrolytes in lithium batteries generates safety issues especially for automotive applications. Ionic liquids due to their amazing thermal stability offer a very interesting alternative as safer electrolytes but some developments are still required in order to use them in lithium battery.**


## CONTEXT

Lithium ion batteries typically use carbonate-based electrolytes which are volatile and flammable; thus safety concerns can limit their usefulness. The replacement of these solvents by ionic liquids (ILs) is under consideration *[A. Lewandowski et al., J Power Sources, 2009, 194, 601]* as they have low vapor pressure and high flash point. They are also good ionic conductors and present wide electrochemical window and high decomposition temperature. *[P. Wasserscheid and T. Welton, Ionic liquids in synthesis, WILEY-VCH, 2003]*

## APPROACH

The development of IL based electrolytes at CEA is addressed through three different axes: 1) Synthesis of specifically designed ILs for batteries application 2) Determination of thermal and electrochemical properties of the most promising ILs and 3) Implementation of IL based electrolytes in prototype.

## RESULTS

Based on strong background in synthesis of ILs at CPE Lyon, a new process has been developed in order to synthesize with quantitative yield highly pure ILs such as pyrrolidinium piperidinium and imidazolium bis(trifluoromethanesulfonyl)imide (fig 1) which is mandatory for their use as solvent for electrolytes. This new chemical pathway has been patented [1] and enables the preparation of innovative structure. [2]

In parallel, a methodology to characterize thermal and electrochemical stability of ILs has been established in order to confirm their interest as safe electrolytes (fig 2). [3] In particular, the nature of generated gases in hazardous conditions like overcharges or car crashes has been determined in collaboration with INERIS. As ILs present different physico-chemical properties compared to carbonates (especially a particular behaviour in terms of wettability of separator), a specific design of prototype cells has been developed using adapted membrane. This work demonstrated the possibility of practical use of ILs based electrolytes in full lithium-ion batteries at industrial scale as shown by cycling tests of prismatic cells (fig 3).

## CONCLUSIONS AND PERSPECTIVES

These developments show the global approach lead by CEA on the use of ILs based electrolytes. A fundemental research project has been carried out to produce and characterize ILs but we are also investigating their integration in full lithium batteries.

## PARTNERSHIP

ESCPE Lyon (Team of Catherine SANTINI), University of Lyon I, CNRS (UMR 5265), UTC-ESCOM, INERIS, Muenster University and SOLVIONIC.


## FUNDING

This project was partly carried out as part of a 7th framework program of EC (ORION project)


**Please note**

Part of this work is done as part of the PhD thesis of Hassan SROUR and Léa CHANCELIER. This work was awarded at the conference of The French Chemical Society.


**References**

[1] Srour , Patent FR1158242, 2011
[2] Srour *et al., Green Chem.,* 2013, 15 (5), 1341-1347
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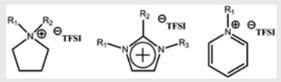

**Fig. 1**
Molecular structure of various ILs

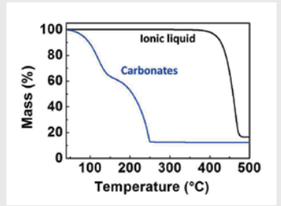


**Fig. 2**
Thermal stability of ILs (in black) vs carbonate based electrolytes (in blue)

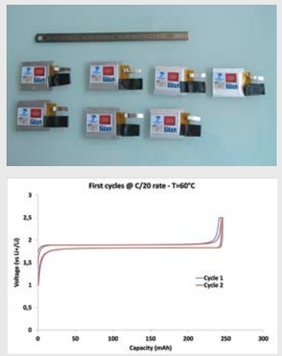


**Fig. 3**
Performances of prototypes using ILs based electrolytes


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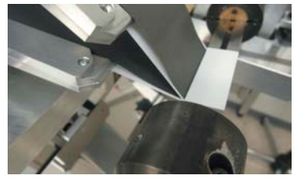
# Development of high energy Li-ion cells for smart devices


## SUMMARY

**On demand demonstrators of high energy Li-ion technologies have been designed, developed and validated for smart devices on the LITEN prototyping and pilot platform.**


## CONTEXT

Lithium-ion batteries need increasing energy densities to increase battery life for devices. The shapes and volumes of cells can be very different according to each individual application and can require specific designs and custom-made components.

## APPROACH

The selection of the chemistry as well as optimization of design and elaboration process of cells enables us to reach our required targets.

## RESULTS

The development of batteries with high mass density (about 215 Wh/kg) was achieved in the **AMELIE FP7 European project.** A high voltage positive electrode (5V spinel) and a graphite negative electrode were developed. The challenge was particularly focused on the optimization of the slurry formulation versus high loading coating (~ 3.2 mAh/cm$^2$) for electrode implementation at pre-pilot scale. Use of molds and shaped guide (designed in the laboratory) allowed making Lithium-ion cells of 2Ah - 215 Wh/kg. The same electrodes in a rigid cylindrical screen (18650 shape cells) lead to 180 Wh/kg. Generally it can be considered that the mass density factor between a rigid packaging and a flexible one is about 0.85.

Three important steps have helped to achieve this result:

- The realization of thick electrodes (Figure 1) to maximize the amount of active material in the cells (tuning formulation, coating process, slitting and calendaring),
- The design and manufacturing of equipment for winding cells in a defined shape, from the general standard 18650 (the most commonly used in laptops) to prismatic cells (Figure 2),
- The design and implementation of a tool for shaping the package (drawing a 4 mm deep multi-layer film), see Figure 3.

AMELIE cells were assembled and electrically tested at CEA, whereas abusive tests were carried out by the partners. Results are encouraging regarding scaling up, but cyclability (limited by high voltage instability) is still to be improved to better meet automotive needs. Within the **PRIAM** FP7 European project vehicle taillights and a panel of innovative road signs incorporating features heterogeneous assemblies on the same plastic substrate were to be produced via a unique manufacturing process in Roll-to-Roll. Three PRIAM demonstrators integrated on a flexible substrate have been made incorporating flexible batteries based on the $LiFePO_4$/G technology. These flexible batteries, designed, dimensioned (shape, stored capacity, power response...) and fabricated in LITEN ( Figures 4 and 5 ) have been successfully tested.

## CONCLUSIONS AND PERSPECTIVES

These developments demonstrate CEA abilities to design Li-ion cells on demand, even when the challenge concerns high energy density or flexible cells. The reproductibility of demonstrators allows envisioning improvements on current processes and components and an industrial phase to the project.


## PARTNERSHIP AND FUNDING

FP7 AMELIE: SOLVAY, VOLVO, Continental, RENAULT, Prayon, Munster University, INPG, ERAS, UNIBO, WWUM, KNUTD,RECUPYL
FP7 PRIAM: CRF (FIAT), CRP, VTT, MICROTEC, AMEPOX, SOLARI



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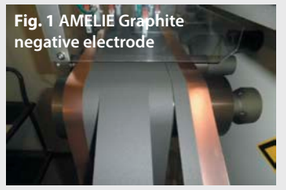

**Fig. 1** AMELIE Graphite negative electrode

**Fig. 2** AMELIE Prototypes assembled before activation

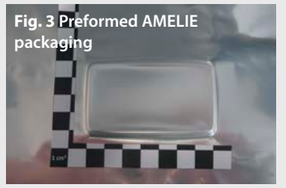

**Fig. 3** Preformed AMELIE packaging

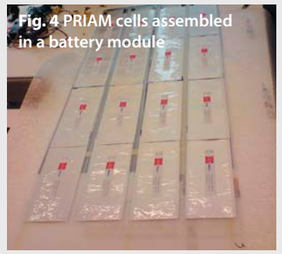

**Fig. 4** PRIAM cells assembled in a battery module

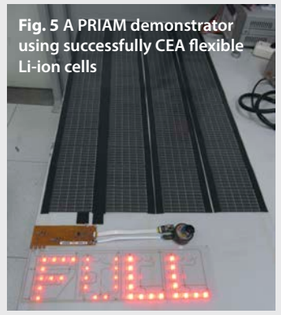


**Fig. 5** A PRIAM demonstrator using successfully CEA flexible Li-ion cells

# Performances of batteries technologies on vehicles



## SUMMARY

**Monitoring is necessary to know the real performances of electric vehicles. The energy delivered by the battery is detailed for aqueous and an iron phosphate lithium ion technologies.**


## CONTEXT

The main four batteries technologies for electric vehicles are lead acid, NiCd, NiMH and Lithium-ion batteries. For the first three technologies, monitoring of electric vehicle indicates significant differences between the supplier specifications synthesis [1] and real use performances.

## APPROACH

Although gravimetric energy (Wh/kg) is a key parameter for battery pack design, the discharge profile cannot be ignored, and real drive tests have to be performed. In several examples, theoretical and practical values have been compared.

## RESULTS

The first study concerned a Citroen AX modification, presented at PCIM conference in 2009 [2]:
The battery pack of Citroen AX was made from NiCd 6V 100 Ah modules (710 Wh, 13.2kg => 54 Wh/kg), assembled to make up a pack of 12 kWh, 280 kg (43 Wh/kg) according to supplier specifications.
However, only 7.4 kWh could be used in a real test drive (61% of specified energy).
In 2009, our laboratory replaced this "12 kWh" NiCd battery by a 10.5 kWh, 138kg (76kWh/kg) $LiFePO_4$ pack.
In the same previous drive test, 10.3 kWh has been delivered, which is 98% of the initial energy. Thanks to this battery swap, the range is now 110 km, compared to 75 km at 90 km/h.
This gap between theoretical and practical energy values, for NiCd batteries, was also published by the Idaho National Laboratory for a Renault Kangoo [3]

A similar second study was performed on the Vectrix scooter [4]: The initial NimH battery (3.7 kWh, 90 kg, 41 Wh/kg) delivered only 3 kWh (33 Wh/kg) in real use.
The following table summarizes the performances:

| | NiCd (Citroen AX) | NiMH (Vectrix) | $LiFePO_4$ (Citroen AX) |
|---|---|---|---|
| specified gravimetric energy of the pack (Wh/kg) | 43 | 41 | 76 |
| measured gravimetric energy (Wh/kg) | 26 | 33 | 75 |
| ratio | 62% | 81% | 98% |

The differences between the real performances and the specifications are due to the test conditions. Aqueous technologies (Pb, NiCd…) have been tested during a three hour discharge (or longer) at constant current. In real use, the current is not constant, and most of all, the battery is discharged in an hour or less. The difference in energy can be explained by the resistive losses of the internal resistance, and by the impossibility to use all the capacitance because of diffusion phenomena limitation.

## CONCLUSIONS AND PERSPECTIVES

Gravimetric energy and the ability of the battery to hold a "real drive test discharge" are key parameters in the battery pack design. The aqueous technologies of batteries are not adapted for electric cars: because of their too low real gravimetric energy on vehicles. Besides safety quality and a high lifetime, Lithium iron phosphate batteries provide 50% to 100% of range improvement on vehicles.


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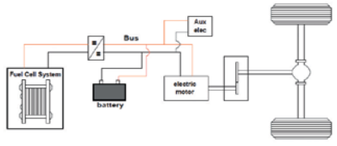
# Validation by HIL of an optimal predictive energy management for an hybrid fuel cell system for automotive application with durability constraints





## SUMMARY

**The electric hydrogen vehicle with a hybrid fuel cell (FC) system and battery is one of the most promising solutions into the carbon free emission transportation mix. To optimize the performances of the system (efficiency and durability) an optimal predictive energy management algorithm has been developed and validated in a real system by fast prototyping on a motor test bench. The results obtained by HIL (Hardware In the Loop) simulation confirmed the previous results obtained by modelling. Moreover, a first step to introduce durability constraints in the EMS algorithms has been successfully carried out.**


## CONTEXT

An electric hydrogen vehicle with a hybrid system (FC and battery) must have an energy management rule to split the power between the FC and the battery function of the vehicle power. In order to optimize the efficiency of the system and also the durability, an optimal online predictive algorithm has been developed and tested by modelling and validated by HIL simulation.

## APPROACH

A power split strategy is implemented in the EMS (Energy Management System) in order to obtain an optimal behaviour for the vehicle in terms of hydrogen consumption and considering the constraints of the system (FC and battery dynamics) [1]. To validate the EMS, a real FC system (5 kW fuel cell with a 2 kWh battery) is directly powered by a 8 kW electric motor tested on a motor test bench. The motor test bench simulates the vehicle inertia and a driving profile is applied.

## RESULTS

Three different strategies were compared: (1) a Rule based method to define the power split between the sources; (2) the optimal predictive algorithm; (3) a dynamic programming (DP) using the graph theory to define the hydrogen optimal consumption path during the drive cycle (offline solution). The tests performed at the motor test bench by HIL simulation (Fig. 1) show that the predictive algorithm performance is very close to the absolute reference (DP).
Moreover, a durability constraint has been added to the algorithm to minimize the effects of ageing if the State of Health (SoH) of the FC becomes too low compare to a SoH reference [2]. Fig. 2 shows some simulation results and the effects on durability and performance. A trade-off between durability and $H_2$ consumption is necessary.

## CONCLUSIONS AND PERSPECTIVES

The results obtained by HIL simulation validate the predictive algorithm. Moreover the algorithm can take into account durability constraints.
The next step is to implement the algorithm in a real FC car and to update the durability constraint laws used.

## PARTNERSHIP

University of Claude Bernard, Lyon I, Ampere laboratory, and IFFSTAR Bron.

**Please note:**
Part of this work has been done as part of the PhD thesis of Ramon da Fonseca. The thesis has been defended in October 2013.


**References**

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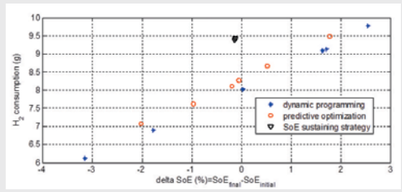
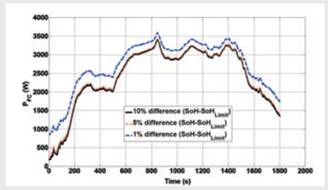



**Fig. 1**
Hydrogen consumption function of the State of Energy of the battery for the different EMS tested in the motor test bench




| $\Delta SoH(t_0)$ | (%)of SOH loss | $g_{H_2}/km$ |
|---|---|---|
| 10 | 0.0502 | 11.9 |
| 5 | 0.0495 | 12.1 |
| 1 | 0.0431 | 13.3 |

**Fig. 2**
Power profile of the fuel cell during urban cycle for different SOH of the fuel cell compared to a reference. The gains of SoH are compared to the loss of FC efficiency.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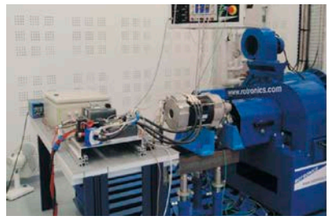
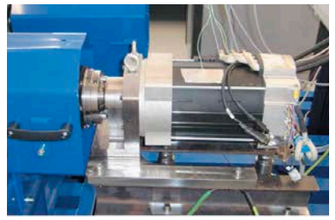
# Test of electric motors with on line road load simulation of electric vehicles


## SUMMARY

**Optimal design of a complete traction system for electric vehicles requires a thermal evaluation of the electric motor. Usage cycles are generally very dynamic and electric motors are able to deliver high transient performances. The evaluation of machines' thermal time response is essential for optimal system design. On line road load simulation is an efficient tool to reach this objective.**


## CONTEXT

When designing a complete traction system for electric vehicles, it is essential to select or to design the optimal motor in order to reach targets in term of system volume and mass and in term of performance and efficiency.
Electric vehicles usage cycles, constituted of temporal profiles of speed and torque, are generally very instationnary and dynamic (Fig. 1).
Energetic efficiency can easily be evaluated with static tests (maps of losses and efficiencies) associated with vehicle energetic simulation (Fig 2.).
Motor performance and reliability are strongly linked with its thermal behaviour. Depending on the motor type, it is generally possible to deliver very high performances, but limited in time.
Being able to estimate thermal time response of motors to a realistic driving cycle gives the opportunity to choose and to size precisely the motor.

## APPROACH

The LIGE electric motor test bench is able to simulate on line dynamic road load profiles. Realistic speed and altitude profiles can be selected and a vehicle model can be defined (mass, SCx, rolling resistance). Realistic road profiles and vehicle model are generally identified on road or on a track by the Monitoring team.
Temperature sensors are added to the motor and the ambient air of the test bench is regulated. Before tests, the motor is macerated during 12 hours in order to obtain an homogenous temperature.
The test bench software applies in real time a mechanical resistance equivalent to what would face the motor in a real vehicle (effect of inertia, vehicle losses, slope)

## RESULTS

We obtain temporal temperature profiles of the motor (Fig. 3), so we are able to evaluate whether the motor is able to deliver the profile performance during the specified time, in correlation with the vehicle range and the battery capacity.

## CONCLUSIONS AND PERSPECTIVES

On line road load simulation is an efficient tool to validate thermal behaviour of a traction system.
A new approach is currently developed based on developing nodal thermal models for electric motors (Fig. 4).
Parameters of these models can be identified with empirical models or with static tests.
On line road load simulation becomes then a validation tool for the model.
Once the models are defined and validated on the bench, it is possible to predict the motor temperature rise on any road load profile.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**References**

[1] M. Gerard, Tests and comparison of two electrical powertrain systems by vehicle simulation test bench and vehicle modeling, *2012 IEEE Vehicle Power and Propulsion Conference (VPPC)*, Seoul (Korea), 9-12 October 2012


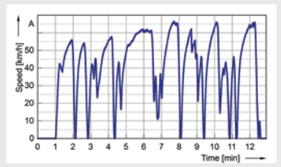


**Fig. 1**
realistic road load profile

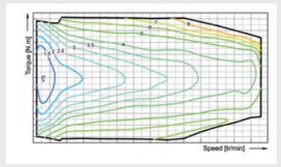


**Fig. 2**
motor efficiency map

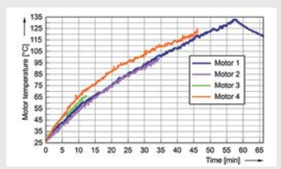


**Fig. 3**
motor temperature rise

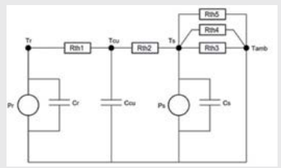


**Fig. 4**
nodal thermal model



# Réseaux électriques, Stockage et Efficacité énergétique
# *Electrical networks, storage and energy efficiency*

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- **Benjamin GUINOT (DTBH) :** Elaboration d'un outil de simulation et d'évaluation des technologies de stockage adaptées aux énergies renouvelables: application à différents scénarios offre/demande – 13/09/2013
- **Pierre PARDO (DTS) :** Stockage d'énergie thermique à haute performance par réaction chimique réversible – 9/12/2013
- **Marion RATEL (DTS) :** Compréhension et minimisation de l'encrassement des trains de préchauffe dans le contexte des raffineries – 5/02/2013

# Demonstration of solar mobility concept at INES


## SUMMARY

**Driven by the need for clean energy sources as well as environment-friendly transportation, photovoltaic energy and electrical vehicles are two emerging vectors towards a more sustainable future. For this purpose, the solar mobility concept has been developed: The aim is to facilitate the massive grid integration of PV and to minimize the impact of electric vehicles on the grid. These vehicles can be charged with PV to reduce greenhouse gas emissions, but they can also, with their battery system, provide grid services. The work carried out at CEA/LITEN shows that the key element for the solar mobility is the Energy Management System (EMS).**


## CONTEXT

The energy sobriety and the environmental protection are two major stakes in our century. The concept of solar mobility which consists of charging the batteries of electrical vehicles (EV) from renewable energy sources: the photovoltaic (PV), can play a key role in this context.

## APPROACH

To demonstrate the feasibility of the solar mobility concept, a demonstrator has been settled at INES in "Bourget du lac". This infrastructure is equipped with a photovoltaic plant of 21 kWc and can welcome up to 12 vehicles simultaneously with 12 charging points. At the same time, a predictive control command system was developed. Its objective is to pilot every EV charge based on forecasts of PV production, an analysis of the energy needs for the EV and take into account the user's constraints: his departure time and his energy needs. The aim of this system is to maximize the use of local PV production during the charge of the EV [1] called solar rate.

## RESULTS

More than 4000 recharges have been completed during the 3 years of experimentation. After the phases of development and stabilization of the Energy Management System (EMS), about 300 days of experiment have been made. Figure 1-a illustrates an example of one day where all the charges were scheduled with the EMS and figure 1-b represents the same day where the absence of EMS was simulated. The solar cover rate passes from 30% to 95% with the use of EMS. During this experimentation period, it was possible to estimate the gain brought by the EMS (blue curve of Figure 2) in comparison with a simulation without EMS (red curve of the Figure 2) on the solar cover of the system regarding the ratio between energy produced and energy consumed.

## CONCLUSIONS AND PERSPECTIVES

These 3 years of experiments show the key role of the EMS in such a system with a final solar cover over 75% of the total needs. Numerous works remain to reach the final goal of the 100% of solar cover. The use of local energy storage systems can be a solution towards this goal.

## PARTNERSHIP

This project was led in partnership with Toyota who supplied the charge points as well as Plug-in Hybrid EVs (PHEV).


## FUNDING

This works was partly carried out as part of a national ADEME program (DHRT2).


**Please note**

Part of this work was carried out during Hervé GUILLOU's Ph D thesis.


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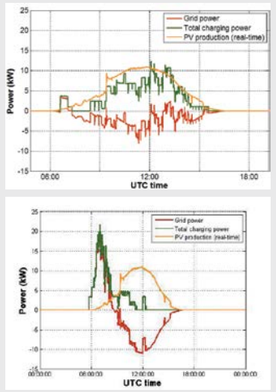


**Fig. 1**
Solar station consumption and production with EMS (a) and without EMS (simulation) (b).

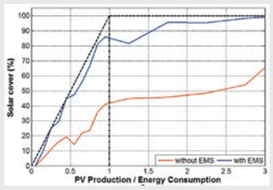


**Fig. 2**
Evaluation of the variation of the solar cover rate according to the ratio between PV production and EV consumption.


## TEAM

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# $H_2$ and LI-ION battery as energy storage for PV stand alone applications: "SENEPY" demonstrator


## SUMMARY

**In order to store electricity produced by renewable energy sources, both batteries and hydrogen appear as complementary solutions. The CEA operates the "SENEPY" pilot demonstrator specifically designed to evaluate the best hybridization between battery and hydrogen storage for PV energy storage.**


## CONTEXT

Batteries are usually used to store intermittent energies, as solar or wind energies, for stand-alone applications or grid management. An alternative way could be Hydrogen Energy Storage ($H_2$ES) where $H_2$ is produced by electrolysis from electricity provided by the renewable energy source, then stored in a tank and converted back into electricity on demand by a Fuel Cell system. It was shown in references [1], [2], [3] that the $H_2$ and battery hybridization used as energy storage for standalone application is the optimal technical and economical solution when the battery operates for short term storage with daily recharges-discharges and the $H_2$ES for long term storage with seasonal recharges-discharges.

## APPROACH

A hybrid system called "SENEPY", with photovoltaic (PV), $H_2$ES and LFP battery coupling, has been developed at laboratory scale (Fig. 1) in order to test, validate and optimize different architectures and different strategies of energy management before implementation into real applications at higher scale. The $H_2$ES is composed of a commercial electrolyzer (0.5 $Nm^3/h$, 15 bars, 230 V AC), a $H_2$ compression and storage system in a 50 liter tank at 200 bar and a homemade 5 kW AC, 230 V Polymer Electrolyte Membrane Fuel Cell (PEMFC) system. An electrical PV panel of 130 $W_{peak}$ is located on the roof of the facility as reference for solar radiation and panel temperature measurements in order to emulate 2 PV modules of 3.5 $kW_{peak}$ each via an automate and 2 AC/DC electrical suppliers. These 2 PV emulators are connected to 2 x 3.5 kW DC/DC MMPT/charger converters linked with homemade LFP battery packaging on a 53 V DC bus. The Direct Current is converted in Alternative Current through a bi-directional 6 kW inverter. The output energy demand is simulated by an AC electronic load up-to 5 kW.

## RESULTS

Fig. 2 shows the SENEPY system in continuous operation during 440 hours. The variation in energy storage levels are represented by the $H_2$ tank pressure (blue line) and the battery state of charge (red line). The green and black curves are the boundary conditions, the PV power respectively and the load power. The overall daily behavior is as follows (Fig. 3): The PV energy supplies in priority the demand. In case of extra PV production, first the battery is recharged, then, once full, the electrolyzer starts to produce $H_2$. In case of a lack of solar energy, the battery is discharged first, then, once empty, the Fuel cell system starts to produce electricity from $H_2$.

## CONCLUSIONS AND PERSPECTIVES

These results will be discussed with respect to those of the study of battery, electrolyser fuel cell durability in order to define the optimum management protocol taking into account both performances and durability.

## PARTNERSHIP

AREVA Energy Storage


## FUNDING

This project was partly funded as part of the French national ANR program (PEPITE) and European EIT/KIC Inno (EES).



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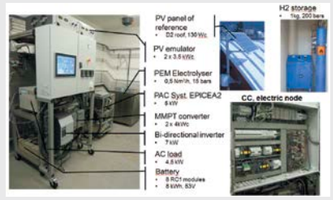


**Fig. 1**
Components of SENEPY system

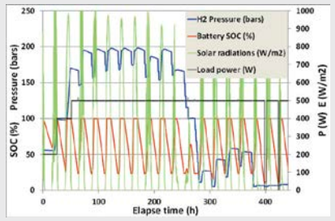


**Fig. 2**
SENEPY system in continuous operation during 440 hours

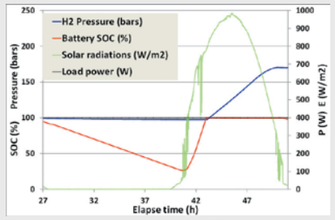


**Fig 3**
SENEPY typical daily behavior


## TEAM

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# Self-consumption: how to minimise the impact of PV in distribution grids


## SUMMARY

**Self-consumption systems will help limiting the impact of intermittent renewable energy in distribution grids. The CEA-Liten is developing a novel PV self-consumption solution, including high performance power conversion and home energy management system.**


## CONTEXT

Electric power from renewable energy sources already exceeds 30% of total installed power in some areas; for instance, in some French overseas territories. Over this critical threshold, power grids can be destabilized due to the non-controllability of these energies. Self-Consumption Systems (SCS) might help manage this issue. They consist of photovoltaic (PV) system associated to batteries and coupled to a Home energy management system (HEMS). SCS maximises local consumption of solar energy by using storage and load management. SCS help to better manage energy production from PV systems by decreasing grid injection in consequently maximising the self-consumption rate.

## APPROACH

CEA is working on several aspects of SCS:
– Load management & Battery management
– Islanding mode
– Multi-source power conversion
The objective is to develop a fully integrated industrial prototype. Herein we give some insights of the ongoing research on SCS.

## RESULTS

A novel power conversion architecture has been developed. It connects battery, PV and the grid and uses only two conversion stages instead of three, so that the overall efficiency is increased. Its architecture is shown in figure 1 (top). Simulation results (figure 1 bottom) show an operation mode in which:

a) The battery DC/DC converter regulates the DC voltage to the value specified by the PV maximum power point tracker (MPPT) within about 100ms by controlling the battery cur-rent.
b) The voltage inverter controls the grid current in amplitude and phase.

The HEMS (HA & Bourry, 2011) manages the electric energy consumption and production of the building. The available flexibilities provided by domestic appliances and storage are used to compute optimal planning for appliance controls. A three layer control approach is used to first compute consumption/production plans and then to dynamically adjust the computed plan to actual consumption/production data.
Simulations of SCS at system level have also been carried out. These steady-state simulations show that SCS helps to decrease power taken from and injected into the grid. Moreover, simulations have allowed CEA to develop advanced HEMS that could take into account multiple energy management strategies.

## CONCLUSIONS AND PERSPECTIVES

SCS is one of the solutions for better managing the energy production of a PV system. Developments undertaken at CEA will lead to a high performance SCS industrial prototype, including power conversion system and HEMS.


## FUNDING

This works was partly carried out as part of a CARNOT program (STAAR project).



**References:**
HA, D. L., & Bourry, F. (2011). Advanced platform for the Home Energy Management System (HEMS) development. In *The 6th Dubrovnik Conference on Sustainable Development of Energy, Water and Environment Systems.*


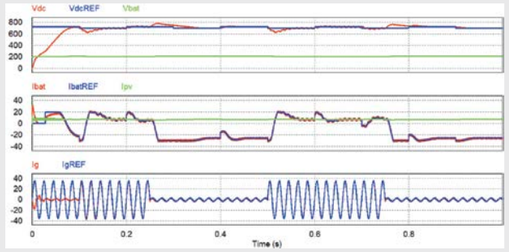


**Fig. 1**
Functional architecture of the power conversion system and associated simulation results.


## TEAM

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# High temperature thermal energy storage




## SUMMARY

**Among the numerous thermal storage solutions, thermochemical storage is a promising way for both high density (up to 400 kWh·m$^{-3}$) and long-term storage (few days to several months). However, it is still a very innovative solution and its feasibility has to be proven at pilot scale. The CaO/Ca(OH)$_2$ hydration/dehydration system is being studied at CEA Liten. The temperature reactions fit well with concentrated solar power plant requirement around 450°C. Hydration and dehydration reactions are implemented in a 1 kW bubbling fluidized bed and the cycling stability is demonstrated over 50 cycles without any reactivity losses. Experimental energy density equal to 166 kWh·m$^{-3}$ is reached.**


## CONTEXT

Thermal energy storage is a key challenge to decouple electricity production from heat availability. If industrial solutions based on sensible and/or latent heat storage systems already exist [1,2], thermal losses limit the heat storage period to around 48 h. Thermochemical storage [3] is a promising solution which could allow both the extension of the storage duration up to several months and the increase of the storage density.

## APPROACH

The CaO/Ca(OH)$_2$ thermochemical storage system is studied in a 1 kW$_{th}$ pilot. The objective is to prove the feasibility of this heat storage solution in a scalable reactor (a bubbling fluidized bed, BFB) and its cycling stability. A numerical model is also used to predict the conversion rate.

## RESULTS

The kinetics of both reactions are first determined in a Thermo-Gravimetric Balance. The experimental results in the BFB reactor demonstrate the feasibility of both dehydration and hydration reactions according to the temperature (from 330 to 510°C) and the absolute humidity conditions (cf. Fig. 2). The process energy efficiency is around 67% and the energy density equals 166 kWh·m$^{-3}$. The reversibility and the cycling stability in the BFB are proven over 50 cycles (cf. Fig. 3).
A two-phase model allows the prediction of the BFB reactor performance during dynamic operation. It is based on the two phase fluidization theory. It can predict both the temperature and the reactant concentration profiles, the conversion rate and the outlet absolute humidity.

## CONCLUSIONS AND PERSPECTIVES

The reaction system involving CaO/Ca(OH)$_2$ was successfully investigated and has demonstrated its potential for thermochemical heat storage applications at pilot-scale. A 10 kW$_{th}$ continuous heat exchanger/reactor is being developed and will be associated to CFD numerical simulations to increase the process performance.


## PARTNERSHIP

AREVA, SHAP (Italy), CSIC (Spain), APTL (Greece).

## FUNDING

This work was carried out in the frame of a European FP7 program (StoRRe) and a Carnot program (CaStoRRe).


**Please note**
Part of this work is done as part of the PhD thesis of P. PARDO.


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[3] Pardo *et al.*, A review on high temperature thermochemical heat energy storage, Renew. Sust. Energy Rev., 2014.


**Fig 1**
Photograph of the 1kW pilot.

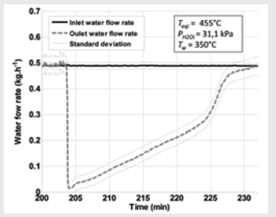


**Fig. 2**
Water flow rate consumption during the CaO hydration reaction.

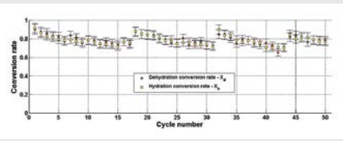


**Fig. 3**
Hydration (Xh) and dehydration (Xd) conversion rates during the cycling study with a $N_2$ fluidization gas.


## TEAM

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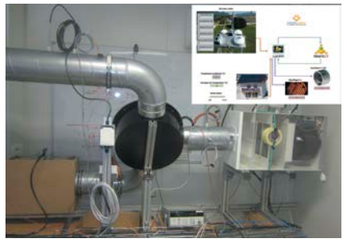
# From theoretical building energy needs to real energy consumption




## SUMMARY

**After the period of building energy software development which permitted mostly to estimate and reduce energy needs the development of near zero energy buildings needs to propose a guarantee of performance. Simulator tools and sensor uncertainties, therefore have to be taken into account.**


## CONTEXT

The theoretical design of new buildings with very low energy needs is no longer a problem. But the actual energy consumption is different from the forecast due to many factors and uncertainties.

## APPROACH

In order to reduce the gap between calculated and actual consumption, we developped the following technology modules: Firstly the identification which allows to highlight the most important parameters in the system. Second is the model reduction, required to optimize the building control strategy. The last important point is the visualization of the building energy performance to help the stakeholder and energy manager to take the right decisions (management, investments).

## RESULTS

The methodology developed for the identification process has been validated thanks to the experimental INCAS house platform. Firstly with static parameters of the building such as thermal characteristics of materials [1] and then with dynamic parameters like weather conditions [2]. The second module, the model reduction and calibration, also uses experimental data to find the better compromise between accuracy and simplicity of the model [3] and has been implemented in control strategies for individual houses. Fig. 1 shows a comparison between several numerical models and measured temperature during 8 weeks. These models were obtained by a particle swam optimization method using less than 14 days of the measured data. The optimisation objective is to minimize mean absolute error between measured internal temperature in the building and the model output. Finally the "user information" module has been developed thanks to the monitoring of 6 social buildings during 2 years. Different levels of output have been defined to help energy managers in their decisions (Fig. 2).

## CONCLUSIONS AND PERSPECTIVES

The assembly of these technology modules enables us to tackle new topics such as "Building energy diagnostic suitcase", performance guarantees and improve the robustness of the conception stage and have synergy from conception stage to energy consumption visualization. One of the next steps is to focus on the district level.

## PARTNERSHIP:

Schneider Electric, CSEM, CSTB, CNRS, Delta-Dore, CEA-LIST, Armines, EDF, INPG


## FUNDING

ADEME, ANR, FP7, Carnot


**Please note**

Part of this work is done as part of the PhD thesis of J. Goffart, M. Rabouille and in some national (Fiabilite, Preccision, GOSPELS), European (Ambassador, Resilient, Performer) or internal (GPE) projects.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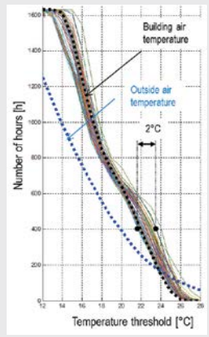


**Fig. 1**
Comparison of experimental and several numerical results using cumulative temperature plot

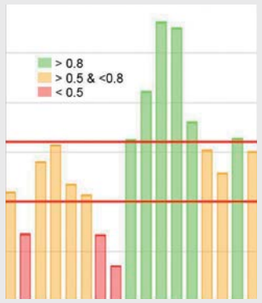


**Fig. 2**
Solar DHW ??production performance monthly ratio from 09/2012 to 01/2014 on a social housing building - GOSPELS project


## TEAM

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# Publications

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## RÉSEAU ÉLECTRIQUE, STOCKAGE ET EFFICACITÉ ÉNERGÉTIQUE

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