# CeFEMA

**Center of Physics and Engineering of Advanced Materials**

## Newsletter Setembro 2014

## Editorial

JOSÉ EMÍLIO RIBEIRO

This is the first number of a CeFEMA publication with bi-annual periodicity. With this publication, we aim to report the activity of CeFEMA to a broad community, be it academic or entrepreneurial, which may be interested in material science and condensed matter physics. CeFEMA is a newly founded center of Técnico, which brings together companies, physicists, chemical and material engineers to do research and production in the area of advanced functional materials. As it is widely recognized, this area plays an essential role in the development and sustainability of modern society as its strategic importance is deemed fundamental by all research and innovation programs at national and international levels, in particular, by Horizon 2020, Research and Innovation Program.

## Desktop Fast Field-Cycling NMR Relaxometer

PEDRO JOSÉ SEBASTIÃO

Nuclear Magnetic Resonance (NMR) is a well-established experimental technique used in many areas of fundamental and applied research. Between 1943 and 2003 the developments associated with NMR deserved the attention of Swedish Academy in six occasions and Nobel prizes in Physics, Chemistry, and Medicine were awarded. Human body imaging is perhaps the NMR application that is better perceived by the general public, but in many areas in academy and industry, NMR is being used extensively in view of the precious information it can provide about the studied systems, with minimum intrusion. In R&D departments of both academy and industries, in many areas (e.g. pharmaceutical, cosmetic), NMR is part of the experimental techniques used in the development and characterization of new materials. NMR studies at high NMR frequencies provide information essentially related to the first neighbors of a given nuclear spin. In the case of molecular systems with self-organizing properties (e.g. liquid crystals, biological systems), or molecules subject to some sort to confinement (e.g polymer nano-composites) some properties of the systems useful for applications can only be investigated considering distances larger than the dimensions of a single molecule. In some cases, this requires the use of NMR equipment operating at frequencies below 10 MHz. The development of NMR equipment operating at low frequencies requires the use of new electromagnets and control systems able to cycle the magnetic with short transients (<3 ms) between different magnetic field levels. This technique is known as Fast Field Cycling (FFC) and allows for the study of the relaxation of the nuclear spins systems at a low magnetic field/frequency while detecting the NMR signal at a frequency where the signal-to-noise figure is favorable. The development of desktop size FFC NMR equipment at IST was motivated by the need to reduce the power consumption usually associated with this type of instrument. A new control system of the electromagnet's power supply and a new type of FFC metal-core electromagnet were developed (see figure).

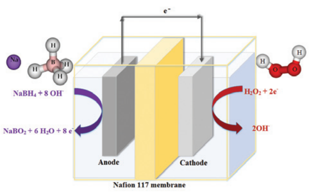
The technology developed was patented in 2007 (PT 103705) and the prototype is unique in the world as it operates with a power consumption of 150W (24V, 6A) in the frequency range 5kHz-8.9 MHz. Due to the low power dissipation and small dimensions an inexpensive air cooling system is used. The NMR console also developed for this prototype presents a user-friendly graphical interface.

The spin-off project "ESPINDAL" was awarded in the "Concurso de ideias de negócio-FIVE 2004". The equipment is operational since 2007 and so far has supported the work of 6 master theses, 8 Ph.D. theses (including Portuguese and Brazilian students), and more than 15 scientific papers published in international journals. The existing knowhow associated with the use of FFC NMR to characterize different material systems has reached a point where it is possible to extend the available experience to other systems, including natural systems or systems with large economical impact in food industry, pharmaceutical applications, polymer, elastomer, and membranes with enhanced properties, etc.. The existing know-how, expressed on the ongoing project of a newer FFC NMR prototype, opens the possibility to collaborate with industrial partners on the optimization of measuring procedures for the study of specific systems, the development of specific NMR equipment to be installed closer to the production lines, or simply the production of FFC NMR equipment.

# Fuel Cells Research at CeFEMA

DIOGO M. FRANCO DOS SANTOS

Fuel cells (FCs) are electrochemical devices that convert chemical energy into electricity. The electron flow is generated from spontaneous redox (oxidation-reduction) reactions occurring at the electrodes. Unlike batteries, as long as fuel and oxidant are supplied to the FC compartments, the device can operate in continuous mode. Typical FCs use hydrogen (H2) as the fuel and oxygen (O2) as the oxidant. However, safety issues and the high costs involved in gas storage in pressurised containers have led CeFEMA researchers to drive their focus to room-temperature liquid-feed FCs. It was almost a decade ago when the materials electrochemistry lab of CeFEMA started its pioneering work in the research and development of the direct borohydride fuel cell (DBFC). It uses a sodium borohydride (NaBH4) aqueous solution as the fuel and hydrogen peroxide (H2O2) as the oxidant. The use of liquid reactants makes the DBFC a promising solution for space, underwater, and specific terrestrial applications where O2 is not available [1]. Initial studies intended to learn about the fundamentals of the anodic oxidation of NaBH4 [2-4]. To decrease the current cost of NaBH4 fuel the group investigated its electrosynthesis [5], which required the development of analytical methods for the NaBH4 determination [6,7]. Next step involved the optimisation of the DBFC operation, by tuning the fuel, oxidant, and membrane compositions [8-10]. For the last few years, CeFEMA researchers have prepared, characterised, and studied new materials for the anode [11-14] and cathode [15,16] electrodes, looking for high electrocatalytic activity at lower prices. The advantages of high energy density and room temperature operation suggest future use of the DBFC for portable applications (e.g., cell phones, laptops).

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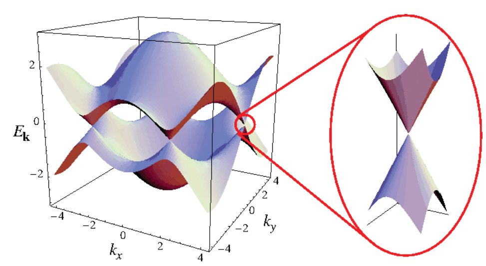
# Graphene: an inside perspective

EDUARDO V. CASTRO

A decade ago, published in the prestigious scientific journal Science after being rejected by the not less prestigious journal Nature, a paper claimed that the thinnest material ever had been produced and measured. That paper gave rise to the 2010 Noble prize in physics, awarded to Andre Geim and Konstantin Novoselov from the Manchester University, who lead the experiments on the material. In retrospect, that paper was a breakthrough in material science, starting a new research area with implications not only in physics, but also in chemistry, biology, and medicine. At first sight, we would expect a very sophisticated method and expensive equipment to be necessary to produce such a material. Not at all! Scotch tape and a graphite chunk are the main ingredients. Not many funding agencies would invest in the idea of pilling off graphite with scotch tape. After a decade, however, many agencies around the world, and in particular in Europe, are giving a lot of money to research in this area. This is the story of GRAPHENE, almost as impressive as the material itself.

Carbon atoms in graphite form one atom thick layers which are very weakly bonded together. That is why we can pill off one of those layers, dubbed graphene, and ultimately that is why we use graphite in pencils. After the 2004 Science paper we became aware of graphene's many superlatives. It is the thinest material and the one with the lightest charge carriers, is the strongest material ever measured, the most stretchable, conducts electricity and heat better than copper, has the highest room temperature mobility, it is almost transparent and yet the most impermeable material, and the list goes on. The material has so many wonderful properties (sometimes it is called "wonder material") that, in the beginning, asking for possible applications sounded like a child which, looking at dolphins' abilities, asks



whether they can be eaten. But the main limitation to applications was the scotch tape technique, which is not scalable. That is why initially the field was mostly driven by fundamental research. As an example, it was known theoretically that charge carriers in graphene should have linear dispersion (see figure) and obey relativistic quantum mechanics. One year after the 2004 Science paper the ultra-relativistic behavior was experimentally confirmed. This time Nature published the result. Actually, Nature even accepted two papers, with the very same result, published back to back in 2005: one from the Manchester group, another from Philip Kim's group, at Columbia University.

Around 2009 the first centimeter square samples were produced using scalable methods. The door was open to real technological applications: supercapacitors due to the very large surface to volume ratio, touch-screens due to flexibility and conducting properties, and because it could replace the expensive ITO, high frequency electronics, flexible electronics, chemical sensors with single-molecule resolution, etc. There are so many possibilities that the European Union selected graphene as one of the first FET Flagship projects, with a budget of EUR one billion, expecting to take graphene from academic labs to the society in ten years.

At CeFEMA, taking profit of the know-how on graphene and other low dimensional materials, and of different backgrounds among its members, we are developing a strategic project in the area: Graphene and Other Low Dimensional materials (GOLDmater). This CeFEMA project is based in four main pillars: synthesis and characterization of graphene and other low dimensional materials, surface engineering using novel two-dimensional materials, study of electronic properties, and theoretical analysis and modeling. Two dimensionality is not restricted to gaphene. Transition metal dichalcogenides and oxides are novel two-dimensional materials with technological interest. These are examples of other low-dimensional materials that will be produced and investigated at CeFEMA under the GOLDmater strategic project. In collaboration with other groups at IST interested in the subject, we plan to make the School a reference in the field.

# Metal laser printing

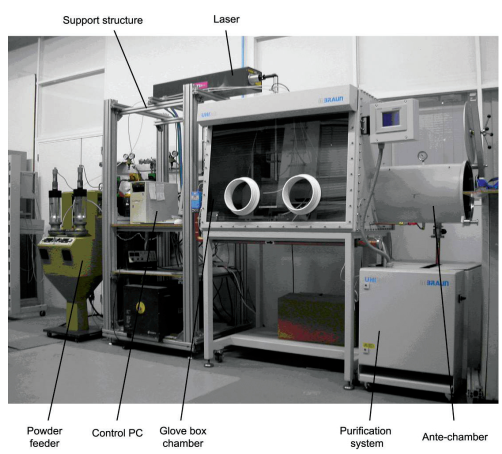
**RUI VILAR**
PRESIDENT OF CeFEMA

## Laser powder microdeposition (metal laser printing) system for the production of customised dental and cranio-maxillofacial implants

Until recently, the processes utilized to produce machine components and tools could be either formative, where a material is shaped into a required form or subtractive, where a material is removed to realize the intended part. The integration of computer design and modelling, along with electronic positioning and measuring systems, lead to the emergence of a third category of productive processes whereby an object is built by the controlled addition of material to form successive layers corresponding to sections of the desired structure. Additive processes of this nature are classified with a wide range of names, depending on the application. Rapid-prototyping is generally used when producing parts for shape visualization or evaluation while rapid manufacture/tooling is used for one-of-a-kind or small series production of functional parts.

Laser powder deposition allows fabricating 3D objects directly from a CAD model by progressively adding and consolidating controlled amounts of feedstock material at precise locations. The underlying principle is the generation of a pool of molten liquid via a focused laser beam into which metallic powder particles are injected, increasing the material volume. The laser beam/material influx interaction zone is scanned over the work piece precipitating the solidification of the melt pool and the formation of a track of deposited material. The 3D overlapping of these tracks allows producing consolidated metal parts of arbitrary shape. The process is fast and extremely efficient, both in material and energy consumption. Since no hard tooling is required, the part's shape can be easily modified without excessive cost, making the process particularly suited for customisation parts, such as dental and cranio-maxillofacial implants.

The machine presented was developed within the European Union funded research project "RAMATI-Rapid manufacture of titanium implants", which undertook an investigation into the feasibility of the use of laser powder deposition based technology for the fabrication of metallic biomedical implants, with a particular focus on small parts such as dental crowns and maxillofacial prostheses. The project en-




*Metal laser printing system developed.*

tailed a collaboration of leading European research institutes in the fields of laser additive manufacture, robotics, process control and biomaterials development and testing.

The laser powder deposition system was based on 200 W CO2 or fibre continuous wave lasers and a coaxial powder micro feeding nozzle deposition head that focuses the laser beam and the powder particles stream onto the same point of the work piece in order to engender material deposition at a sub-millimetre scale. A glove box and gas purification system was used to maintain an inert argon atmosphere during processing.

The work piece motion relative to the laser beam/powder stream is provided by five axes positioning under computer control. Synchronization of the positioning tables, powder feeder and laser is provided by software written in Delphi which communicates with each component by sending analog and digital signals.

As layers of material are successively deposited at high temperatures heat accumulation lowers the temperature gradient in the part and, therefore, less laser energy is required to generate a melt pool of the same geometry. To compensate for this situation a closed-loop control system was developed to monitor the melt pool dimensions and adjust the laser power to keep this parameter constant. The melt pool is monitored by measuring the radiation emitted by the hot metal in a certain near-infrared wavelength range using a photodiode. The photodiode signal is used to keep deposition conditions constant via a control algorithm.

The microdeposition system was tested in the production of Co- and Ti-alloy parts. A simulated dental crown fabricated by deposition of successive layers using Ti6Al4V powder is shown.


Ti6Al4V dental crown manufactured by metal laser printing.

*In memoriam of Chris Meacock who carried out part of this work as a PhD Student.*

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