Sensible **sensors**

Air pollution is a major threat to human health, but electrochemical sensors to detect harmful gases in the environment currently use lead, which is itself toxic. **Dr Didier Fasquelle** is part of an initiative developing a new generation of innovative, lead-free sensors that will significantly reduce their environmental impact

The Lead-Free Oxides for Gas Detection (Oxydes sans plomb pour la détection de gaz – OSPÉGAZ) project aims to replace existing lead-based electrochemical sensors with lead-free oxide alternatives for the detection of gas. Could you provide a brief overview of the project?

Many commercial gas sensors are composed of electrochemical cells, especially those used in the detection of flammable gas. Industrial firms producing these lead-based sensors can consume more than a ton of lead per year. This is a concern because lead is one of the most hazardous and polluting raw materials; it affects the central nervous system and has the potential to induce infertility and cancer.

In 2008, the modified European Restriction of Hazardous Substances (RoHS) directive appeared, prohibiting the use of hazardous substances like lead, cadmium and mercury. As such, there is an urgent need for lead-free components in Europe, and industry is now trying to produce electronic components and devices which comply with RoHS standards. In line with this, OSPÉGAZ aims to develop gas sensors and new systems of instrumentation without lead for monitoring indoor air quality in houses and public buildings, as well as the detection of dangerous toxic and flammable gases in industrial sites.

How will your new approach enable the detection of flammable gases without the risk of toxic contamination?

When working on new environmentally friendly technologies, you must verify that your replacement of hazardous substances with alternatives will benefit both public health and the environment. Therefore, the study and development of our sensors for the detection of flammable and toxic gases includes specific environmental goals. The same consideration will be taken when carrying out tests with gas, which will be undertaken by our industrial partner Simtronics SAS, because their methods comply with the necessary security standards.

What are the differences between catalytic and semiconductive sensors, optoelectronic cells, photoelectric sensors and pyroelectric sensors?

Catalytic and semiconductive sensors are passive. Passive sensors are where variation of the resistance is measured. Another similarity is that both of these classes work at high temperatures, generally from 200-500 °C. They are both the simplest in terms of their instrumentation systems and also the cheapest gas sensors to produce.

Optoelectronic, photoelectric and pyroelectric sensors are active because the detection cell or element is associated with diodes or transistors. Optoelectronic devices need three different parts in the detection head: a light emitter, a sensitive element and a receptor, which is generally a phototransistor or a modified field effect transistor (FET). In this case, the sensitive element is located between the emitter and the receptor or is embedded in the gate of the FET.

Could you discuss the multidisciplinary approach adopted for the project?

This project needs many complementary skills that are contributed by different partners. The synthesis of the different materials used in the sensitive element of the sensors is based on physical and chemical approaches. The packaging and electronic systems development is based on electronic and engineering approaches. Testing the sensors with different gases and under different environmental conditions, and subsequent analysis of the experimental results, is based on physical and mathematical approaches. Finally, data needs a complete overview to understand what is happening in the sensor and how the functioning of the detection system could be improved – and of course, project management is important to ensure the schedule is adhered to.

The advancement of gas detection technologies will open up the possibility of identifying a broader range of gases. How will lead-free oxides facilitate this process?

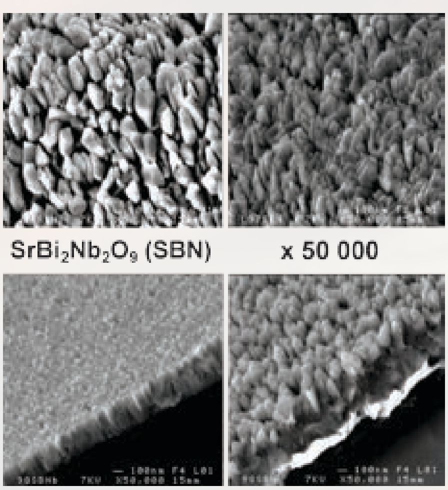
Lead-free oxides are a really broad family because they can be developed using one, two, three or four different raw materials. A simple oxide is generally made with titanium, tin or tungsten oxide; binary oxides include barium titanates or potassium niobates; ternary oxides are doped binary oxides where the dopant is the third material. Therefore by combining several raw materials – modifying the identification process and deposition conditions of the final product – you are able to control the physical and electrical properties of the final oxide layer that will be the core of your sensor. All these process parameters enable us to use a wide range of sensors.

Lead-free gas **detection**

Many devices for detecting flammable gases include raw materials that have the potential to harm both the environment and human health. The **OSPÉGAZ** detection project based at the University of Littoral Côte d'Opale in France is developing new, environmentally friendly sensor systems to combat the issue

AIR POLLUTION IS a significant threat to human health worldwide. In France, one solution proposed by the 2nd French National Environment and Health Action Plan (NEHAP 2) is to reduce the aqueous and atmospheric emissions of several priority substances, including lead. If such an initiative is to be enforced, there is a need for methods of detecting these substances in the environment.

Most gas detection devices currently use lead-based electrochemical sensors and are therefore themselves toxic to the environment. Since the end of the Second World War, industrial development has resulted in increased levels of pollutants such as lead in a broad range of food products. This in turn has led to increased incidence of cardiovascular and respiratory diseases, as well as cancer, kidney disease and nervous system disorders. To ensure the mitigation of future environmental damage, and to fall in line with restrictive legislation concerning lead or other pollutants use, new technologies and instrumentation to monitor indoor and outside air quality and detect dangerous gases are required.



Scanning Electron Microscope (SEM) photos of SBN thin films with various microstructures. Views from above and cross-sections are given.

LEAD-FREE DEVICES

To address this, researchers from the University of Littoral Côte d'Opale in Calais and from the University of Rennes are working on the development of innovative integrated instrumentation systems for the detection of various environmental pollutants. The Lead-Free Oxides for Gas detection (Oxydes sans plomb pour la détection de gaz – OSPÉGAZ) project aims to create sensors that are lead- and platinum-free, and which are capable of detecting explosive gases, protecting against toxic hazards and monitoring air quality. Platinum is avoided for its cost, which continues to dramatically increase each year, while lead is avoided due to it toxicity. Under the guidance of Dr Didier Fasquelle, OSPÉGAZ's new devices will be developed in accordance with NEHAP 2's recommendations and tested under exposure to their identified priority substances. They will be made from low-cost materials using cost-effective manufacturing techniques, and will be used to monitor the air quality in public buildings, although simpler and cheaper adaptations could potentially be produced for individual houses. The hope is that they will ultimately replace existing gas sensors: "Lead-free materials are really an environmental choice as green technologies must be developed to eliminate hazardous substances from all current electric applications in future," Fasquelle points out.

The project involves studying and manufacturing different materials; characterising them physically and electrically; and then manufacturing sensors that will be directly integrated into detection cells. The entire process from the design and synthesis of oxides to the integration of the sensors within the final packaging involves a number of individual steps and extensive scientific expertise. In order to fulfil the range of skills required, OSPÉGAZ is highly multidisciplinary and comprises three partners – two laboratories and the industrial firm Simtronics SAS, one of the leading French gas detection companies.

OPTIMISING MANUFACTURING

Central to the group's work has been the development and optimisation of the manufacturing processes used to deposit thin and thick films of lead-free oxides onto different kinds of substrate. It is the interactions between gas molecules and these microstructured films that result in the detection of gas. Together with academic and industrial partners, he has experimented with a wide range of oxides and the use of different deposition techniques under different conditions, including sol-gel, screen printing, pulse laser deposition and sputtering. The need for low cost, adjustable film composition, deposition onto substrates of differing natures and an easy transfer to industry led the team to retain the sol-gel technique for the fabrication of thin films and serigraphy for thick films. Despite their reduced sensitivity, screen-printed thick films are ideal due to their value for money and ease of production.

After more than a year's work, OSPÉGAZ has developed a range of microstructured film surfaces for their semiconductor gas sensors and different inks for catalytic sensors. Preliminary electric characterisations were carried out on the films to allow the team to adapt the input electronic board to each sensor. The films were then embedded into sensor packaging comprising an analogic board which transduces the gas detection into an electric signal, and an instrumentation system developed by Simtronics SAS which incorporates a high resolution analogic-to-digital converter and a digital unit for the storage and numerical treatment of digital data.

Finally, Fasquelle's team has tested their sensors under different conditions at Simtronics SAS. The firm's equipment allows them to choose the type of gas, gas flow, duration of exposition, operating temperature of the sensor and exposure conditions of the detection system, such as temperature and moisture. In this way, they were able to define all experimental conditions and compare the results from their sensors to currently available commercial

LEAD-FREE OXIDES FOR GAS DETECTION (OXYDES SANS PLOMB POUR LA DÉTECTION DE GAZ – OSPÉGAZ)

OBJECTIVES

- To develop lead-free, environmentally friendly replacements for current gas detection systems
- To explore new potential lead-free materials, as well as improve the sensitivity of existing materials
- To explore new technologies for gas sensing

KEY COLLABORATORS

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FUNDING

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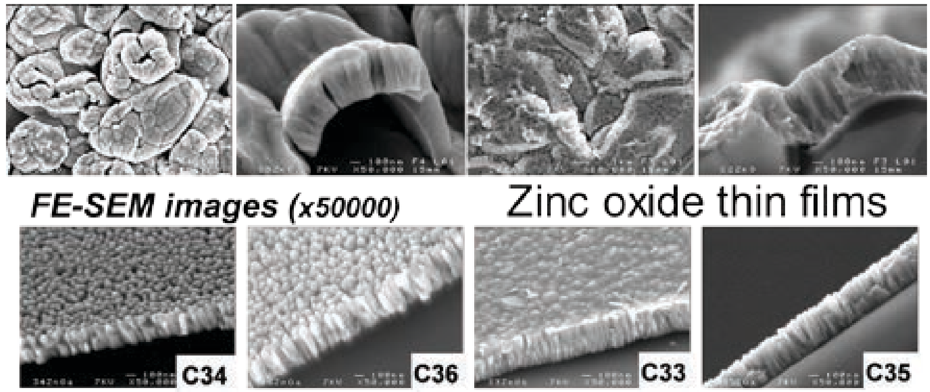
DR DIDIER FASQUELLE is an Associate Professor and full supervisor of thesis works at the University of Littoral Côte d'Opale. His main works focus on functional ceramics and thin films (sol-gel), electrical characterisations in wide temperature and frequency ranges, piezoelectric and pyroelectric properties, and more recently on gas sensors and cathode materials for solid oxide fuel cells. He has published 70 papers.



SEM photos of zinc oxide thin films with four different microstructures. Views from above and cross-sections are given.

devices. The effectiveness of their sensors was also deduced from experimental measurements such as sensitivity, response and recovery time, selectivity, sensor stability and detection periodic cycling. All tests using flammable and toxic gases are carried out under advanced safety conditions to protect the project's engineers and researchers.

A NEW GENERATION OF SENSORS

Fasquelle now intends to further develop the detection capabilities of his lead-free oxide sensors. The team is working on the optimisation of the sensor input circuits, the DC-DC converter used to power the system's heater and the dimensions of the sensors, in order to improve their gas detection capabilities and allow for adjustments to the temperature range, and will experiment by modifying different parameters in the construction of the sensors as well as in the operating conditions. "The project aims to highlight different kinds of lead-free materials that can be sensitive when exposed to these gases, but the pathways for increasing the sensitivity of the current sensors are also being explored for some selected materials," Fasquelle explains. These improvements will eventually lead to the sensors' use for the detection of an extended list of gases, as specified by NEHAP 2.

Furthermore, the properties of the lead-free oxide films OSPÉGAZ has developed can be translated to other applications, enabling the creation of a new generation of innovative gas sensors that utilise various technologies, such as catalytic passive sensors and optoelectronic cells with an integrated pyroelectric sensor. Such devices are much more efficient in terms of selectivity – the sensor's ability to continue detecting the designated gas, even under exposure to a mixture of different gases. The cheapest sensors, based on catalytic and semiconductive behaviours, are currently not particularly selective. To extend the project even further, Fasquelle plans to investigate different technologies dedicated to gas detection: "These technologies open up an even broader field of study and investigation for a base material, including the ability to detect a larger range of gases," he enthuses. The next stage will centre around the optimisation of the properties (sensitivity, selectivity and response times), dimensions and electric consumption to develop specific sensors for Simtronics.

Top left: Photos of electronic boards.
Bottom left: a sensor with and without a head grid.
Right: Simtronics' detection head.

NEHAP 2'S GOALS

AT THE HEART of OSPÉGAZ's work is the desire to improve overall environment and health safety, not only in France but worldwide. The 2nd French National Environment and Health Action Plan (NEHAP 2) was produced following the Grenelle Environment roundtable talks, and it provides the wider framework that the project's work fits into. It outlines France's four-year plan for environment-related health risk prevention, and some of the solutions it has proposed include:

- Reducing emissions into the air and water of six toxic substances: mercury, arsenic, polycyclic aromatic, hydrocarbon, benzene, perchloroethylene and polychlorinated biphenyl by 30 per cent by 2013
- Reducing concentrations of fine particulate matter in the ambient air by 30 per cent by 2015
- Introducing health warning labels on building and decorating materials that release the highest levels of harmful substances into buildings
- Improving procedures for testing substances
- Identifying and dealing with environmental blackspots which are most likely to lead to exposure to toxic substances