Novel NOx Sensing Technology
Determining value by looking at patent potential and possible partnerships.

by
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Thesis Supervisor

Accepted by ______  

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Chair, Departmental Committee on Graduate Students

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ABSTRACT

Professor Michael Cima in MIT’s Department of Materials Science and Engineering has developed a new approach for sensing NOx (nitric oxide and nitrogen dioxide), and Christophoros Vassiliou, a Masters of Engineering student in Electrical Engineering, is working with Cima on the development of the technology in the lab. The novelty of the electrochemical sensor is that it employs a molten alkali carbonate electrolyte as opposed to sensors with solid electrolytes, which are generally used.

While the science of the sensor is still under development, Cima has targeted diesel engines for implementation. The purpose of this thesis was to assess the value of the technology and suggest possible actions. By looking at the structure, trends, and competitive drivers in the market for automotive gas sensors, I have outlined the plausibility and grounds for obtaining a patent and also suggested possible licensing opportunities or partners to fund reduction to practice. Such companies include Ceramatec, Bosch, and City Technology.
ACKNOWLEDGMENTS

This thesis would not have been possible without the guidance of my advisor, Michael J. Cima, nor without much valuable insight from Christophoros Vassiliou. Many thanks to David Roylance for encouraging a finance major with an interest in materials science to pursue the MEng program and also to Carl Thompson, Eugene Fitzgerald, and Kathy Farrell for their valuable assistance in helping me complete the program.

I, of course, give my sincere gratitude to my family and friends for supporting and putting up with me throughout. Also, a special thanks to Katie Huffman and Nalani Gupta, without whom I could have never made the transition into the field.
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I. Introduction

Professor Michael Cima in MIT’s Department of Materials Science and Engineering has developed a new approach for sensing NOx (nitric oxide and nitrogen dioxide), and Christophoros Vassiliou, a Masters of Engineering student in Electrical Engineering, is working with Cima on the development of the technology in the lab. The novelty of the electrochemical sensor is that it employs a molten alkali carbonate electrolyte as opposed to sensors with solid electrolytes, which are generally used.

Cima has targeted diesel engines for implementation of the technology because the high temperature combustion environment, while providing better fuel efficiency, also results in increased NOx production compared to gasoline engines. The use of a catalytic converter to reduce the NOx requires a sensor to (a) signal when the converter is fully saturated and (b) monitor if the converter is working properly. Cima believes that the MIT sensor is superior to the existing technology available to the automotive industry in terms of size, simplicity, cost, sensitivity, selectivity, and durability, all of which will be compared and discussed in greater detail.

While the science of the sensor is still under development, I have analyzed the business opportunities and potential for the technology by determining the

- Structure, trends, and competitive drivers in the market for gas sensors
- Plausibility and grounds for obtaining a patent
- Possible licensing opportunities or partners to fund reduction to practice

Using this information which I obtained from patents, patent applications, journal articles, scientific papers, company websites, press releases, and firsthand interviews, I have suggested possible patent claims and also elucidated reasons to consider partnering with Bosch, Ceramatec, or City Technology.
II. Background on gas sensors

Where and why are sensors necessary?

Gas sensors are required to detect and limit the amount of harmful gases such as NOx, hydrocarbons (HC), and CO emitted into the environment from a variety of sources. Sensors are especially important in light of tightening EPA emissions regulations over the next five years. In addition to harmful gases, gas sensors, such as oxygen (lambda) sensors and CO₂ sensors, are used to assess environments and dictate necessary adjustments. Examples of markets and applications for various gas sensors are listed in the table below.

Table I. Exemplary Applications and Markets for Chemical Sensors.

<table>
<thead>
<tr>
<th>Market/application</th>
<th>Examples of detected chemical compounds and classes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive</td>
<td>O₂, H₂, CO, NOₓ, HC, VOC, Bacteria, biologicals, chemicals, fungal toxins, humidity, pH, CO₂, NH₃, amines, humidity, CO₂, pesticides, herbicides, O₂, glucose, urea, CO₂, pH, Na⁺, K⁺, Ca²⁺, Cl⁻, bio-molecules, H₂S, Infectious diseases: ketones, anesthetics gases, pH, Cl⁻, CO₂, O₂, O₃, H₂S, SOₓ, CO₂, NOₓ, HC, NH₃, H₂S, pH, heavy metal ions, Indoor air quality: toxic gases, combustible gases, O₂, O₂, CO, HC, NOₓ, SO₂, CO₂.</td>
</tr>
<tr>
<td>IAQ</td>
<td></td>
</tr>
<tr>
<td>Food</td>
<td></td>
</tr>
<tr>
<td>Agriculture</td>
<td></td>
</tr>
<tr>
<td>Medical</td>
<td></td>
</tr>
<tr>
<td>Water treatment</td>
<td></td>
</tr>
<tr>
<td>Environmental</td>
<td></td>
</tr>
<tr>
<td>Industrial safety</td>
<td></td>
</tr>
<tr>
<td>Utilities [gas, electric]</td>
<td></td>
</tr>
<tr>
<td>Petrochemical</td>
<td></td>
</tr>
<tr>
<td>Steel</td>
<td></td>
</tr>
<tr>
<td>Military</td>
<td></td>
</tr>
<tr>
<td>Aerospace</td>
<td></td>
</tr>
</tbody>
</table>


Existing technology

Gas sensing involves several different types of sensing technology. Below is a list of the various general categories of gas sensors, characterized by their detection method.

- Metal-oxide-semiconductor gas sensors
- Electro-oxide-semiconductor gas sensors
- Spectroscopy of surface reactions
- Metal phthalocyanine gas sensors
- Colorimetric methods of gas detection
- Infrared gas detection
- Optical fiber gas sensing
- Surface acoustic wave sensors for atmospheric gas monitoring

²
The MIT sensor is an amperometric, molten electrolyte, electrochemical sensor which means that a gas analyte chemically interacts with elements of the sensor, providing an electrical signal proportional to the gas concentration. Although the specific thermodynamics and kinetics of the reaction are unknown at this point, we do know that the phenomenon occurs. In general, electrochemical gas cells ionize gas molecules at a three-phase boundary layer (atmosphere, electrode of a catalytically active material, electrolyte). Examples of electrode materials are platinum for CO and gold for NO₂. The ion current (e.g. H⁺, O⁻, Cl⁻, F⁻) through the electrolyte to the counter electrode serves as the signal in amperometric-type cells as is the case with the MIT sensor, which contains two gold electrodes. The other type of electrochemical sensors are potentiometric cells in which the potential difference generated between the electrodes by different partial pressures on both sides of the cell serves as the signal. Most oxygen sensors in car exhausts are of this type.³

III. How does the MIT sensor work?

The structure

The construction of the MIT sensor has changed significantly throughout the time I have worked with Cima and Vassiliou. Initially, the MIT sensor was comprised of two gold electrodes surrounded by alumina, a stainless steel casing, and a molten alkali carbonate electrolyte made of a mix of Na₂CO₃, K₂CO₃, Li₂CO₃. A picture of this version is shown below in Figure 1.

![Figure 1: First design of the NOx sensor (schematic by Vassiliou).](image)

Unfortunately, the alumina interfered with the sensing capabilities, so Vassiliou decided to eliminate the existence of a substrate to prevent such interactions. Various versions of the sensor followed which
Vassiliou will be outlining in his M.Eng thesis later this year. In general, though, the size of the sensor decreased throughout development with the goal of creating a stable prototype to be used in the lab to test the impact of variations in electrolyte compositions and atmospheric conditions. The final version of the sensor is still underdevelopment, but the goal is to keep the structure and geometry as simple as possible to eliminate unfavorable interactions with contaminants that would taint our signal.

*Measuring NOx concentration?*

Current is passed through the gold electrodes shown above. When NOx gas enters the sensor, it interacts with the molten carbonates. The exact mechanisms of the reaction is still unknown, but Cima and Vassiliou believe that the reaction is fast and then slow because initially the NOx dissolves in the electrolyte and then the later signal corresponds to the actual chemical reaction between the carbonate and NOx. Resistance is measured because it is a reverse function of gas concentration as can be seen from the data plotted below.  

IV. Necessary scientific work

As I mentioned earlier, the structure of the NOx sensor, pictured and described briefly above, is still being tested and perfected. Cima and Vassiliou are considering several other methods for packaging the technology in order to decrease the size and increase durability. As mentioned earlier, once they create a prototype that works consistently, then factors like electrolyte composition and electrode material can be tweaked to improve sensitivity and
cost. Currently, the gold electrodes are the most expensive component (comprising about 95% of the material costs). However, Vassiliou hopes to test other electrode materials such as nickel in the near future to try to reduce material costs.

V. Advantages of MIT sensor

The quality and value of gas sensors are measured based on the following five attributes:

- Cost
- Size
- Simplicity
- Sensitivity
- Durability
- Selectivity (Cross sensitivity)

The key advantage of the MIT sensor is its ability to detect NOx concentrations as low as 12 ppm. Sensors currently under development at NGK only detect as low as 100 ppm. However, Ceramatec, a materials company that will be discussed in greater detail later, boasts sensitivity down to 1 ppm. A table of typical sensitivity ranges for various target gases is given in Figure 3 to illustrate the superiority of the MIT sensor.

As seen from the cost analysis, the gold electrode is the most significant contributing factor (not considering the cost of labor, which will most likely be significantly reduced in actual manufacturing). Although other gas sensors do use gold electrolytes, particularly NOx sensors, others use cheaper materials such as nickel. Despite the cost of the electrode, the overall simplicity of the MIT sensor bodes well for its production costs because many existing gas sensors involve
complex multilayer systems, series of chambers, pumps, and other characteristics that increase overall fabrication costs.

VI. Market Analysis for Gas Sensor

Structure

The global market for gas sensors and gas metering equipment including secondary instrumentation was estimated to be $2.8 billion in 2004 and expected to rise at an average annual growth rate of 5.9% to $3.8 billion in 2009 according to an extensive report on the gas sensor market performed by Business Communications Company, Inc. in April of 2005. The full text of the report includes a review of major products and applications and the future effect of gas metering and gas sensors/monitors; examination of the industry’s structure; analysis of competitive aspects; market evaluation by product type and application with forecasts to 2009; examination of international trade; profiles of more than 100 major players in the industry. Unfortunately, the report is not available to the public ($4,000 full text), so I compiled much of the same information from other sources.8

The need for gas sensors essentially began in the late 1950’s in the coal mines. Since then, the industrial and commercial applications for gas sensors has increased dramatically, causing the gas sensor industry to expand into hundreds of companies with a range of size and specialties accounting for the thousands of variations in gas sensors. Some companies have large sensor divisions and research arms (NGK, Delphi, Bosch, TI), some focus solely on developing and manufacturing sensors for various applications (City Technology and Ionotec), and other companies that require sensors for their products also design and produce them (Honda, Volkswagen).

Although research and development occurs within many companies, the knowledge pipeline relies heavily on cooperation with universities across the globe. Companies provide research funding and share resources with academia. For example, 77% of UK universities were collaborating with industries for the development of gas sensors in 2001.9

Market trends

As mentioned earlier, more stringent emissions regulations such as those set forth in the 1990 Clean Air Act Amendments and similar regulations in Europe and across the globe
have fuelled the increased demand for gas sensors. This increased demand has created a need for smaller, low cost sensors with greater sensitivity. The graph below shows the market development of different types of gas sensors. As can be seen, electrochemical sensors are currently widespread, which means that the market is already very developed and competitive.

![Market Development Graph](http://proquest.umi.com)

As can be seen from the graph above, which is also supported by several articles on the future of gas sensors, the new wave is actually infrared sensors, particularly MEMS gas sensors. Such sensors can offer key benefits for sensing target gases, such as low cost when made in high volumes, low power consumption, compact size, and ability to readily integrate with signal conditioning electronics. MEMS gas sensors have not yet made a profound impact on the gas sensor market, due to such factors as competition from well-established sensing technologies, such as electrochemical and metal oxide semiconductor gas sensing devices, and the time required to generate user acceptance of newer technology. However, the proliferation of MEMS gas sensors will largely rest on their ability to penetrate the high-volume markets for gas sensors such as automobiles.¹

In general, recent years have seen many changes to the industry: several companies have been acquired by larger groups; new companies have been founded; new technologies are being commercialized, with varying degrees of success; new applications are emerging;
and the academic research effort seems to go from strength to strength. However, the general industry sentiment seems to be that technology will be more effectively exploited through the development of lower cost products aimed at specific applications. The excerpt below gives an industry recap and prediction for the demand for gas sensors in various sectors.  

**2002 Sensor Review Market Forecast by Industry**

The chemicals and pharmaceuticals industries continue to provide growing demand for industrial gas sensors. These industries are extremely lucrative and competition is high. Some caution should be taken however, as the chemicals industry is showing signs of moving investment to more economically viable regions such as Eastern Europe, Asia and South America, placing future revenues in jeopardy.

The petrochemical and oil and gas refinery industries are expected to represent an important area of growth over the next few years. After recent oil price slumps, these industries appear to be on the road to recovery and prices are slowly increasing. Past troubles in the oil industry have demonstrated the importance of investing in technology, such as gas sensors, which help to improve efficiency and save energy.

Waste and incineration represents a relatively small application for gas sensors but the sector is anticipated to undergo significant growth as efficiency and emissions monitoring considerations become more important. Growth is also expected in food and beverage industries, particularly for dissolved carbon dioxide and food storage monitoring. Another growth area for industrial gas sensors is environmental monitoring, fuelled by growing concerns for more environmentally sound production practices and the introduction of climate change levies.
VII. Business Plan: Extracting Value

In an attempt to fund the development and reduction to practice of the MIT sensor, Cima signed a nondisclosure agreement and discussed the technology with NGK, a Japanese-based company with a worldwide presence and a product line of gas sensors for automobiles. Despite their initial interest in the sensor, they decided not to pursue the technology. Therefore, there is a need to research and pursue other options.

The following section outlines my recommendations for the best way to extract value from the MIT sensing technology based on my research into the market for gas sensors (makers, buyers, consumers); the structure of the gas sensing industry (those who make sensors and those who use them in various systems); emerging technologies in gas sensing; and key attributes driving competition.

First, Cima and MIT should try again to find a partner in industry to help fund the reduction to practice of the sensor and also determine its realistic market value. Although NGK decided to pursue their own technology, they did acknowledge the novelty and promise of the MIT sensor. I have given suggestions for companies which might be interested in licensing the technology in the future, but should first be contacted as potential partners in development. In the process of finding a partner for development, Cima should also try to obtain a patent on the MIT sensing technology and based on my analysis of existing patents and applications, I have summarized possible claims.

A. Obtain a patent

As Lita Nelson of MIT’s Technology Licensing Office stated, the first step is to file an invention disclosure, which Cima has already done. Next, Cima and MIT must obtain a patent on the MIT sensing technology. Looking at patents and applications filed for “gas sensors” and “gas analyzers,” I sought to find a niche for the MIT sensor. In order to do this, I tried to outline the basis of existing patents while keeping in mind that the broader the patent for the MIT sensor, the better.

According to Alan Gordon, at MIT’s TLO, before a patent can be obtained, a prior art search must be conducted with Mary Pensyl. I have already begun such a search and my findings are reported below. Next, the TLO will decide to patent the technology based on discussion with inventors about whether it has been reduced to practice (which the MIT
sensor has not); it has commercial value (based on competitive advantages and various industry needs); it can be protected; and if it is likely that MIT will be able to license the technology. If the TLO believes that the MIT sensor meets these criteria, then they will assign an attorney who will contact the inventors and proceed to draft and file a patent application.

In order to determine the patentability of the MIT sensor, I looked at hundreds of patents for gas sensors with various attributes to determine what the MIT sensor can and cannot claim. An ideal sequence of claims is given. After which, I outline what the MIT sensor actually CAN and CANNOT claim.

*Ideal claims sequence*

Molten electrolyte for measuring gas concentration → electrolyte material → gas sensed → application → structure

*What the MIT sensor CAN'T claim ...*

1. Use of a liquid electrolyte (not in general or in a gas sensor)

   The following patents have already made this claim.

   Electrochemical toxic gas sensor - An electrochemical toxic gas sensor comprising a housing; a working electrode, a counter electrode, and a liquid electrolyte within the housing.

   **Patent 6,080,294** Assignee: Atwood Industries Filed:1998
   Gas sensor with dual electrolytes - A gas sensor for measurement of a gas in an environment comprising, in combination ... a liquid electrolyte.

   **Patent 6,791,737** Assignee: Saint-Gobain Glass France Filed:2001
   Electrochemical device - Electrochemical device involving a multilayer comprises a layer made of an ionically conductive material in the form of an aqueous liquid or of
an anhydrous liquid or based on polymer(s) or on a gel(s). The patent also indicates that this system is used in a gas sensor.\textsuperscript{11}

2. Use of a molten carbonate electrolyte in a gas sensor

Although no US (only a Japanese) patent has been filed on the above, the MIT sensor cannot claim this because it is prior art. The following journal article based in research done at Nagoya University in Japan explains the use of a molten electrolyte in a CO\textsubscript{2} sensor: "Double-cell carbon dioxide sensor based on Li---K molten carbonate with electrochemically-supplied CO\textsubscript{2} - O\textsubscript{2}.” Journal: Sensors and Actuators B: Chemical.\textsuperscript{12}

In addition to Nagoya University, research on electrochemical sensors using liquid carbonates is being performed at Strathclyde University where they are working on a CO sensor that “consists of three electrodes immersed in a liquid electrolyte(a non-metallic liquid that conducts electricity, usually through acids or dissolved salts).”\textsuperscript{13}

\textit{What the MIT sensor CAN claim . . .}

1. Molten carbonate electrolyte for any gas sensor except CO\textsubscript{2}

Other than the prior art mentioned above, which only cites the use of molten carbonates in CO and CO\textsubscript{2} sensors, no other patents or articles that I found mentioned the use of a molten carbonate electrolyte in an electrochemical gas sensor for any other target gases, particularly NOx.

2. Particular structure of the sensor

Throughout the development of the sensor, Vassiliou has experimented with various constructions; however, as I mentioned earlier, the structures used are mainly for use in the lab to test the composition in the electrolyte and the performance in various atmospheres while eliminating noise generated by intricacies in geometry. Despite the simplicity of the structure, the MIT sensor has one distinct characteristic: there is no substrate.
**Description of Prior Art**

- Patents and articles mentioned earlier
- Electrochemical sensors using solid electrolyte
  
  There are thousands of patents on the above, which are differentiated based on materials (electrode, electrolyte), structure, target gas, and structure.
- Molten carbonate electrolytes used in fuel cells
  
  A fuel cell is a device that generates electricity by a chemical reaction. Similarly, the reaction between the gas and the electrolyte in the sensor is what generates a potential when current is applied via the electrodes. There are several different types of fuel cells (alkali, molten carbonate, phosphoric acid, photon exchange membrane, solid oxide). Molten carbonate fuel cells (MCFC) use high-temperature compounds of salt (like sodium or magnesium) carbonates (chemically, CO\(_3\)) as the electrolyte. Knowing this, Cima decided to use a similar electrolyte in a NOx sensor.\(^{14}\)

**B. Why not a start up?**

The MIT sensor is a very specific product, targeted toward use in diesel engines. Also, the opportunity to expand the technology and create more IP is limited. In addition, there are already several large, established companies in many of the industries using gas sensors as was already discussed in the competition section. Finally, Prof. Cima is not interested in starting a company based on the technology. In fact, he stated from the onset that he believed the sensor was simply a product, not an entire business.

**C. Partnerships recommendations (3)**

**Company:** Ceramatec (http://www.ceramatec.com)

**Industry:** Specializes in ceramic electrochemical systems

**Description of the company:** Ceramatec is an advanced materials company that specializes in ceramic electrochemical systems such as ioni
cally conductive membranes, solid oxide fuel cells, and electrochemical drug delivery systems. Located in Salt Lake City, Utah, the company was originally founded as a contract R&D firm by two professors from the
University of Utah in 1976 and initially worked with Ford Motor Company the development of a sodium-sulfur battery. Acquired by Elkem in 1989, Ceramatec spun off several companies from solid-state ionic developments. One example of such companies was Maxtec, which focused on novel ceramic oxygen sensors. However, in 2000 the company "returned to its entrepreneurial roots as a U.S. small business when Dr. Ashok Joshi acquired Ceramatec from Elkem in a management buyout, and became the new owner, President & CEO" (http://www.ceramatec.com/companyinfo) Now the company has over 100 employees, sales of $8.5 million, and "strives to forge new strategic alliances and develop new products and companies dedicated to commercializing their products."15

Why would they be interested in the MIT sensor: Their history, along with the fact that they are currently developing the NOxTrac™ NOx sensor for use in engine exhaust systems, makes them an excellent candidate for a partnership. I found 60 patents and 2 patent applications with Ceramatec as the Assignee and their website also gives the breadth of their patent portfolio (http://www.ceramatec.com/patent/patent.php). Specifically, patent 5,401,372 elucidates the development of the NOx sensor made of an electrochemical cell with a solid electrolyte. However, one of the problems that they encountered was contamination from sulfur. Ceramatec has taken steps to deal with this issue and currently has a patent application (#20050161340) which discusses how to prevent sulfur from interfering with catalysts designed to remove hydrocarbons and nitrogen oxide from motor vehicle exhaust.11

Cermatec presented more detailed specifications of their NOx sensor at the Diesel Engine Emissions Reduction (DEER) Conference in San Diego, CA in September of 2004. The table on the next page is from this presentation.
Specifications of Ceramatec's NOx sensor

<table>
<thead>
<tr>
<th>Specification</th>
<th>Units</th>
<th>Value Targeted at End of R&amp;D</th>
<th>Value Obtained to Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>90% Response Time</td>
<td>Seconds</td>
<td>&lt;1</td>
<td>1-3s</td>
</tr>
<tr>
<td>Detection Range</td>
<td>ppm NOₓ</td>
<td>1-1500</td>
<td>1-1500</td>
</tr>
<tr>
<td>Resolution</td>
<td>ppm NOₓ</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Use Temperature</td>
<td>°C</td>
<td>500-600</td>
<td>500-600</td>
</tr>
<tr>
<td>Cross Sensitivity</td>
<td>N/A</td>
<td>Low cross-sensitivity to SO₂, H₂O, CO, CO₂</td>
<td>Very low cross-sensitivity to CO, CO₂, H₂O; SO₂ must be less than 15 ppm</td>
</tr>
<tr>
<td>Oxygen Range</td>
<td>%</td>
<td>0 to 21%</td>
<td>0.01-21%</td>
</tr>
</tbody>
</table>

In the same presentation, Ceramatec indicated that they are “actively seeking partners for NOx oxidation catalyst technology development and commercialization.... Types of partnering agreements include joint development agreements, technology transfer agreements, and licensing agreements.”

**Company:** Bosch (www.bosch.com)

**Industry:** Automobiles

**Description:** With global sales of over €40 M in 2004 (25.3 M of which stemmed from their automotive technology division), Robert Bosch is one of the world's top makers of automobile components, employing over 149,000 people. Bosch holds over 50 patents for gas sensors in diesel exhaust systems and continues to develop sensor technology. Their Automotive Electronics division works on sensors and control devices for motor vehicles, which help make driving safer, cleaner, cheaper and more comfortable.

**Why would they be interested in the MIT sensor:** With competitors moving manufacturing operations to low wage regions, Bosch is going to be looking for ways of reducing production cost, making the MIT sensor attractive. In addition, Bosch has the infrastructure and supply chain connections to bring the NOx sensor to market. In
looking at auto parts sellers, Bosch is one of the major producers of oxygen sensors. Cima has actually already contacted Bosch who expressed interest, but a meeting has not yet been scheduled.

**Company:** City Technology (http://www.citytech.com)

**Industry:** General (including automotive, emissions, industrial and domestic safety, medical, indoor air quality)

**Description:** Devoted solely to the development and production of gas sensors, this UK-based company located in Portsmouth, England has a global presence in almost every industry requiring sensors. Slightly larger than Ceramatec with 250 employees, City offers a wide range of sensors for detecting oxygen, an extensive range of toxic gases, combustible and explosive gases & vapors, and VOCs. According to their website, their four divisions (Gas Sensing - Sensors, Gas Sensing – Instrumentation, Automotive and Special Products, and Safety and Analysis) produce over 200 different types of sensor for 20 different types of gases.

City Technology was founded in 1977 by four scientists working at London's City University to capitalize on novel oxygen sensing technology. The company grew and expanded the breath of their products and then in 2000 City Technology was purchased by First Technology, a UK based international group who manufacture products that play important roles in improving safety and protection of people and their environment. Now they have a worldwide presence and produce over 1.5 million sensors annually.19

**Why would they be interested in the MIT sensor:** City Technology is one of Europe’s leading suppliers of electrochemical gas sensors and exports globally to 48 countries. The company not only makes sensor for many applications, but also for an array of gases, including automotive applications involving NOx. In addition, they have actively collaborated with universities in the past.16

City gave specifications for their automotive sensors (NO and NO2 separately). Those charts are given below for comparison to the MIT NOx sensor.19
Specifications for City’s NO sensor

Performance Characteristics

- **Nominal Range**: 0-5000ppm
- **Inboard Filter**: To remove effect of SO₂ in gas stream
- **Expected Operating Life**: Two years in air
- **Output Signal**: 0.05 ± 0.01 µA/ppm
- **Resolution**: 1ppm
- **Temperature Range**: -20°C to +55°C
- **Pressure Range**: 800 - 1100mBar
- **Pressure Coefficient**: 0.01% signal/mBar
- **Tₚ Response Time**: <15 seconds
- **Relative Humidity Range**: 15% to 90% non-condensing
- **Typical Baseline Range**: 0 to +12ppm equivalent (pure air)
- **Maximum Zero Shift**: 30ppm equivalent (+20°C to +40°C)
- **Long Term Output Drift**: <5% signal loss/year
- **Recommended Load Resistor**: 10 Ω
- **Bias Voltage**: +300mV
- **Repeatability**: 2% of signal
- **Output Linearity**: Linear

N.B. All performance data is based on conditions at 20°C, 50%RH, and 1013mBar

Specifications for City’s NO₂ sensor

<table>
<thead>
<tr>
<th>SPECIFICATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heater resistance at 21°C</td>
</tr>
<tr>
<td>Operating heater resistance at 410 ± 30°C</td>
</tr>
<tr>
<td>Baseline sensor resistance in clean air at 21°C 50%RH</td>
</tr>
<tr>
<td>'LG' 13 ± 7kΩ</td>
</tr>
<tr>
<td>Gas sensitivity, Rₙₕₑₜₑ as ratio 400ppm carbon monoxide 1ppm nitrogen dioxide 500ppm hexane</td>
</tr>
<tr>
<td>'LG' 4.5 - 10</td>
</tr>
<tr>
<td>'G' 2.0 - 4.0</td>
</tr>
<tr>
<td>Detection range carbon monoxide nitrogen dioxide</td>
</tr>
<tr>
<td>Recommended sensor measurement voltage</td>
</tr>
<tr>
<td>Ambient operating temperature range</td>
</tr>
<tr>
<td>Storage temperature</td>
</tr>
<tr>
<td>Ambient humidity range</td>
</tr>
<tr>
<td>Typical power rating</td>
</tr>
<tr>
<td>Maximum power rating (at -40°C)</td>
</tr>
<tr>
<td>Maximum current consumption (at -40°C)</td>
</tr>
<tr>
<td>Integrated filter technology</td>
</tr>
<tr>
<td>Lifetime, thermal cycles 21°C to 500 °C</td>
</tr>
</tbody>
</table>

1. Oil free compressed air supply with activated carbon filtration
IX. Conclusions

The MIT sensor is obviously very early in development. However, based on my findings, there should be opportunities to collaborate with industry to reduce the sensor to practice, at least for the detection of NOx in diesel exhaust systems. Although, the technology is NOT a candidate for a broad, overarching patent, it does have unique qualities, elucidated above. Even though the market for electrochemical gas sensors is fairly saturated, if Cima can prove that the MIT sensor is significantly better, particularly in terms of cost and sensitivity, then it increases the commercial potential of the sensor and likelihood of it being licensed. In addition, I believe that Ceramatec, Bosch, and City Technology are all plausible candidates for a partnership based on the histories and current products.
X. References


5. Vassiliou, C and Cima, M. Presentation given to NGK.


