

Chemical Detection Using Electrically Open Circuits Having No Electrical Connections

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Abstract

This paper presents investigations to date on chemical detection using a recently developed method for designing, powering and interrogating sensors as electrically open circuits having no electrical connections. In lieu of having each sensor from a closed circuit with multiple electrically connected components, an electrically conductive geometric pattern that is powered using oscillating magnetic fields and capable of storing an electric field and a magnetic field without the need of a closed circuit or electrical connections is used. When electrically active, the patterns respond with their own magnetic field whose frequency, amplitude and bandwidth can be correlated with the magnitude of the physical quantities being measured. Preliminary experimental results of using two different detection approaches will be presented. In one method, a thin film of a reactant is deposited on the surface of the open-circuit sensor. Exposure to a specific targeted reactant shifts the resonant frequency of the sensor. In the second method, a coating of conductive material is placed on a thin non-conductive plastic sheet that is placed over the surface of the sensor. There is no physical contact between the sensor and the electrically conductive material. When the conductive material is exposed to a targeted reactant, a chemical reaction occurs that renders the material non-conductive. The change in the material's electrical resistance within the magnetic field of the sensor alters the sensor's response bandwidth and amplitude, allowing detection of the reaction without having the reactants in physical contact with the sensor.

Introduction

Chemical sensors have been employed for a large variety of applications such as bio-sensing, environmental analysis, food analysis, clinical diagnostics, drug detection, gas detection, toxicity detection, and detection of chemicals that could be used for warfare or terrorism.^{1,2} Many of the sensors have a specific synthesized receptor that selectively binds with an analyte of interest. Another sensor approach is to have a specific chemical reactant react with a target reactant. Each approach produces a measurable change that is discernable via an electrical component such as a capacitor or resistor. Sensor arrays coupled with pattern recognition techniques are being used to mimic mammalian olfactory systems.³ Unlike "lock and key" sensing, each sensor in the array is chosen to respond to a number of different chemicals without the need to be highly selective to any particular chemical.³ Each sensor has a different degree of response to similar analytes. Differentially responsive arrays use the "cross reactivity" pattern resulting from each analyte upon all sensors in the array.³ To date, all chemical sensors have two common features. One feature is that the sensors are closed circuits with electrical connections. Another feature is that the receptor/reactant and the analyte physically contact one part of the sensor circuit.

Chemical sensor innovation is driven by either the infrastructure innovations such as microelectromechanical or wireless sensors or innovations/discoveries in chemistry such as the development of Carbon-60 resulting in carbon nanotubes and the development of conductive polymers. NASA has recently developed newer sensor baseline circuit designs that are magnetic field response sensors requiring no physical connections to a power source or acquisition hardware. These are damped simple harmonic oscillators formed from inductors electrically connected to capacitors in closed circuits. Damping results from the inherent resistance in the circuit. The sensors are powered via external oscillating magnetic fields and respond with their own damped oscillating magnetic fields whose frequency, amplitude and bandwidth correspond to magnitude of the measurand.⁴ The method of powering and interrogating magnetic field response sensors presented in Ref 4 facilitates the measurement of the magnitude of multiple unrelated physical quantities. Ref 4 also discusses how magnetic field response sensors can be developed for specific measurements. Application of these to chemical sensing has been presented in Refs 5 and 6 including gas sensors using multiwall carbon nanotubes- SiO₂, for detection of CO₂, oxygen and ammonia.⁶

We present preliminary results of chemical detection using a sensor design that was originally developed by NASA for identifying multiple damage events to inflatable space structures. The baseline sensor circuit is shown in Fig 1a. The external harmonic magnetic fields used for powering the sensors and the responding harmonic magnetic field of the sensor used for interrogation eliminate the need for electrical connections to a power source and to interrogation hardware. The sensor geometry eliminates the electrical connections necessary to have a harmonic resonator. Therefore, in lieu of an electrical circuit made from a collection of electrical components and electrical connections, sensing can be achieved using stand alone two-dimensional geometric patterns of electrically conductive material.⁷

The sensor provides all the functionality of a traditional closed circuit having a capacitor, inductor and resistor without requiring electrical connections. The sensor baseline design is the simplest completely functional circuit that can be manufactured. Since it is a single electrical component, there is less manufacturing cost and time. Another advantage of open-circuit sensors are electrical connections are eliminated and in doing so, there is no longer a single point on the circuit that if damaged destroys the functionality of the circuit. If the sensor is damaged (torn, punctured or ripped), it still functions but with a different frequency range. Although the initial objective of this study was to develop a wireless chemical detection system for detecting gases such as NH₃, CO, CO₂, O₂, H₂ and CH₄ for detecting fuel leaks using the methods presented in Refs 4-5, the sensing methods have unique attributes making them attractive for broader chemical sensing requirements. A discussion of two approaches for using open-circuit chemical sensors follows.

First Approach - Reactant Placed Directly upon Circuit

In 2006, we demonstrated, to our knowledge, the first electrically open-circuit chemical sensor. The baseline sensor circuit, Fig 1a, was coated with a 150 nm layer of silicon nitride followed with a layer of polyaniline, Fig 1b. The excited sensor's magnetic field response frequency has a reference baseline of 21 MHz after being coated with the reactant, polyaniline. It was exposed to 0.1 % concentration of ammonia gas. The sensor's frequency shifted 0.6 MHz from its baseline when exposed. The shift in frequency demonstrated that the open-circuit sensor when coated with a reactant to specifically react with a chemical (for which identifying the presence of the

chemical is an objective) could serve as a sensor. When the targeted reactant chemically mixes with the dielectric originally coated on the sensor, a new chemical product is formed having a different dielectric than the reactant thus shifting the sensor's response frequency. If the reactant to be placed on the sensor is electrically conductive, an electrically insulating layer is placed between the electrical trace and the reactant. The combination of insulation coating thickness and reactant conductivity must be such that the sensor's magnetic field does not get attenuated by the conductive material. The electric field of the sensor must also be sufficiently present in the reactant that when exposed to an external chemical (e.g., gas), the frequency shift is discernible. In another set of tests, sensors coated with tin-oxide were exposed to oxygen. One sensor's response frequency and magnitude changed 0.72MHz and 3.7 dBm, respectively. The other changed 0.32 MHz and 1.9 dBm.

Second Approach - Reactant Separated From Circuit

Another method of using the sensor exploits the change in electrical conductivity of the reactant/receptor when it is exposed to the analyte. The genesis for the second approach was the following hypothesis. The excited sensor's magnetic field response frequency, amplitude and bandwidth, when the excitation conditions are fixed (antenna position, orientation, output amplitude and frequency), are dependent upon the electrical conductivity of any material placed within its magnetic field.⁸ If the reactant used to identify the presence of the targeted reactant is electrically conductive and the resulting chemical reaction between the two results in an electrically nonconductive product, then the chemical reaction can be detected without having either reactant in physical contact with the sensor. When an electrically conductive material is placed inside the magnetic and electric fields that propagate toward it, energy is lost from the fields and appears in the material in the form of Eddy currents. If the fields incident to the material are $B_{RX}(T, r_i)$ and $E_{RX}(T, r_i)$ at a distance r_i from the sensor, the fields on the other side of the material will be

$$B_{RX}(T, r_i + \Delta z) = B_{RX}(T, r_i) e^{-\Delta z / \delta} \quad (1)$$

$$E_{RX}(T, r_i + \Delta z) = E_{RX}(T, r_i) e^{-\Delta z / \delta} \quad (2)$$

The field attenuations are dependent upon the conductive material's thickness, Δz , and skin depth, δ . The skin depth is the distance over which an electromagnetic wave will be attenuated by a factor of e . The skin depth, δ , is dependent upon the material's relative permeability, μ_r , electrical conductivity, σ , and the wave frequency.⁸

$$\delta = \left(\frac{2}{\omega \sigma \mu_r} \right)^{1/2} \quad (3)$$

This loss of energy alters the sensor response. Less energy in the magnetic and electric fields means less inductance and less capacitance, respectively. The response amplitude is also lowered. This is reversed if the material is taken away from the field. Now if the material's conductive property changed, instead of changing the position of conductive material in the field, the sensor response would change as shown in Fig 2. This would result in less energy loss (higher amplitude and smaller response bandwidth, $\Delta\omega$, at the same reference level, ΔA). If a

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substance reacts with the conductive reactant and the resulting product is non-conductive, the sensor would lose less of its energy resulting in a decreased response bandwidth and increased response amplitude. Those changes for a specific reaction could be used to indicate that the chemical reaction occurred. If the material's conductivity changes, the skin depth changes resulting in a different sensor response frequency and amplitude. If the change results in decreased conductivity, the response amplitude will increase and the frequency will decrease.

To demonstrate the method, a chemical reaction that used a conductive polymer that when exposed to the analyte resulted in a non-conductive product. Measurement of the response before and after the reaction was used to determine if there was a change in conductive properties and therefore a chemical reaction. The conductive reactant was kept at both a fixed position and orientation with respect to the sensor. As in the first method, the conductive polymer, polyaniline, was used. Fig 1c shows the baseline circuit with a thin plastic sheet coated with polyaniline placed on top of it. Table 1 shows the results of exposing four samples of the sensors coated with polyaniline to ammonia. Both response amplitude and bandwidth change with exposure to ammonia. The bandwidth changes are more pronounced – the bandwidth is reduced by approx 33% because the resulting material is less electrically conductive. The response difference between the samples is due to non-uniform coating of the polyaniline. This method has been demonstrated for identifying gaseous ammonia using polyaniline as the reactant. Results have indicated a response change is discernible with a separation of 1 cm between the reactant used to identify gaseous ammonia and the sensor.

Test No	Response Amplitude Increase, (dBm)	Response Bandwidth Reduction at 10 (MHz)
1	2.2	0.78
2	7.5	0.92
3	5.3	0.66
4	7.9	1.06

Table 1. Experimental results of exposing the sensor to ammonia.

Future Work and Concluding Remarks

Preliminary results of using of geometric patterns of electrically conductive open-circuits having no electrical connections for chemical sensing have been presented. The sensors are simple harmonic oscillators that are electrically excited using external oscillating magnetic fields and once electrically active respond with their own magnetic fields thus eliminating the need for any external connections. The goal of this study was to determine if the sensors could be used for chemical sensing. Two unique approaches demonstrated that they could be used for sensors. The first method tried was direct placement of the reactant, polyaniline, on the sensors. Sensors with tin-oxide were also exposed to oxygen using the first method. In another approach, a conductive polymer – polyaniline was placed on a transparency film so that there was no direct physical contact between the sensor and the polyaniline. When exposed to ammonia, the sensor response bandwidth decreased 0.78 – 1.06 MHz, an approximately 33% decrease. The bandwidth change was a result of the conductivity decreasing with the exposure. The electrically conductive polyaniline placed in proximity to the sensor absorbs some of the magnetic field from

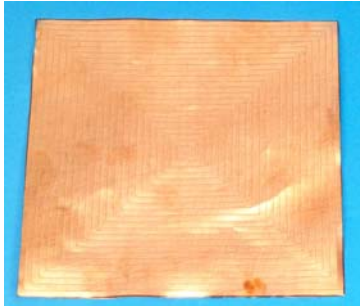
the “sensor” resulting in the sensor having less inductance and an energy loss. When exposed to the ammonia, the conductivity decreases resulting in the sensor being able to store more energy when excited hence it has a lower bandwidth and higher amplitude for the same excitations conditions. The sensor is different from previous chemical sensors in use and in the literature in that it is an electrically open circuit and does not require any electrical. Eliminating the electrical connections and using a single electrical component (electrical trace) reduces the sensor’s probability of failure and a single component is a far simpler design to produce and far less expensive to manufacture. An advantage of the second method is that the sensor trace need not be in contact with the chemical reactant thus allowing each to be physically on either side of a non-conductive barrier.

The work we have done makes it possible to have sensors or sensing arrays that could be deposited directly onto any non-conducting surface in lieu of depositing sensors onto intermediary substrates, completing all electrical connections and then bonding them to the surface. Future work should focus on quantifying the detection sensitivity to key parameters such as sensor geometry, receptor coating thickness, temperature, etc. There should also be studies to determine what chemicals can be detected using the presented methods.

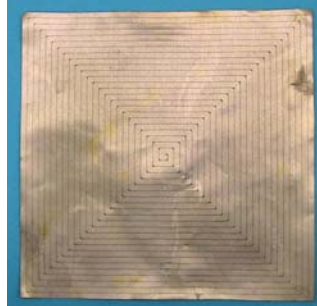
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a. Electrical conductive open circuit trace with no electrical connections



b. Electrically conductive trace coated with silicon nitride and then polyaniline.



c. Electrical trace beneath a transparency coated with polyaniline.

Fig 1 An electrically conductive spiral trace with the spacing between the traces reduced to increase its capacitance was used as a new baseline sensor circuit

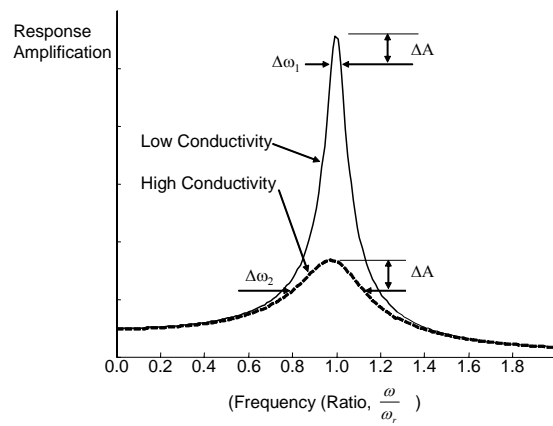


Fig. 2. Magnetic field response resulting from sensor proximity to surfaces having high electrical conductivity and low electrical conductivity