

Detection of Hypergolic Fuels with a Chemicapacitive Sensor Array

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Accurate and reliable detection of hypergolic fuels is a vital component to the Kinetic Energy Interceptor (KEI) module of the U. S. Missile Defense Agency. Seacoast Science has developed a sensor that uses micromachined capacitors to measure the dielectric constant of a group of selectively absorbing materials. The interaction between target analyte and polymer modifies the dielectric properties (capacitance) of the material. Using an array of commercially available polymers, functionalized polysiloxanes and polycarbosilanes of varying architecture (starburst, hyperbranched, and dendritic) both substituted and unsubstituted hydrazines (hydrazine, monomethyl hydrazine, and unsymmetrical dimethylhydrazine) and nitrogen dioxide (nitrogen tetroxide mimic) were detected in the presence of water vapor or hydrocarbons as interferents.

Introduction

There is a growing threat of foreign enemy states and terrorist organizations acquiring ballistic missile technology to use or threaten to use against the United States or our allies. Because of the instability of certain rogue nations and terrorist agents, the threat of massive retaliation may not be a sufficient deterrent (1). Part of the MDA's proposed protection scheme is the Kinetic Energy Interceptor (KEI) to be used in the Boost Phase Defense. For the KEI system, the ideal missile design uses a liquid fuel initiator (monomethyl hydrazine (MMH) – fuel; nitrogen tetroxide – oxidizer). The overarching goal of this research was to satisfy the concerns of the current policy of the United States Navy (USN) that prohibits these chemicals on USN vessels. A detection system that addresses the concerns of the USN both from the possible explosion danger and the toxic adverse effects from MMH would assist in this process. A chemical sensor suite based on microelectromechanical capacitor technology that allows for alarm detection of high levels (LEL) of hypergolic compounds within the canister and missile nose and a fixed sensor array that will detect MMH and NO₂ at toxic (PEL) levels might enable MDA to eventually field the KEI on USN platforms.

MEMS-based Chemicapacitive Sensor Array

The core technology detailed herein is a sensor array or an “electronic nose.” This term can encompass many different types of sensor technologies (2) with a common goal, namely the mimicry of mammalian olfaction (3). The receptors in the nasal cavities of mammals do not detect individual chemicals selectively, but use many, perhaps thousands of types, of partially selective receptors, which absorb the chemicals being inhaled (4, 5). These receptors may respond strongly, weakly, or not at all, resulting in patterns, which the brain learns to identify as a specific odor. Many chemicals will make these receptors fire; the key is that the relative intensities are different for different odors.

The brain then determines if that chemical “smell” has been encountered before. Most electronic noses have the same three components: a method to sample or move the target molecules to a set of sensors; an array of different sensors, i.e. transducers each with the ability to absorb chemicals with its own type of “chemical selectivity;” and an electronic “brain” or set of algorithms that translate what the sensors detect into distinguishable patterns and then interpret the patterns to determine chemical composition and concentration. This method allows the sensor to detect a chemical even when interfering agents (e. g. humidity) may be present. Just as the sense of smell must be trained or learned, the electronic nose system must be exposed to different combinations of chemicals to be trained to identify these patterns.

MEMS fabrication methods developed during the past few years has dramatically reduced the size, weight, and cost of current chemical detectors. MEMS technology involves fabricating mechanical systems such as sensors on silicon in a manner similar to that used to manufacture modern electronics. Since MEMS technology is compatible with many circuit production processes, it may ultimately be possible to produce an entire detector system including the detector, gas sampling system, preconcentrator, and electronics on a single silicon chip (6).

Since 2003, Seacoast Science, Inc. has been working on the research and development of capacitive gas sensors for several applications such as monitoring of homes and offices and defense related applications. Target analytes and applications for these sensors include: volatile organic compounds (VOCs) (7); furnace emissions; hydrogen monitors (for electric transformer failures); mold (*Stacybotrys*, *Aspirgillus*) toxins; fumigants (ClO_2 , H_2O_2); chemical warfare agents (CWAs) (8); explosives; and toxic industrial chemicals (TICs). In general, each sensor chip measures 5 x 2 mm and contains between 8 and 16 capacitors constructed using surface micromachining techniques. The capacitors are individually coated or “filled” with different analyte-sensitive coatings as needed. Both a novel interdigital transducer (IDT) and a parallel plate structure were used in the study (Figure 1).

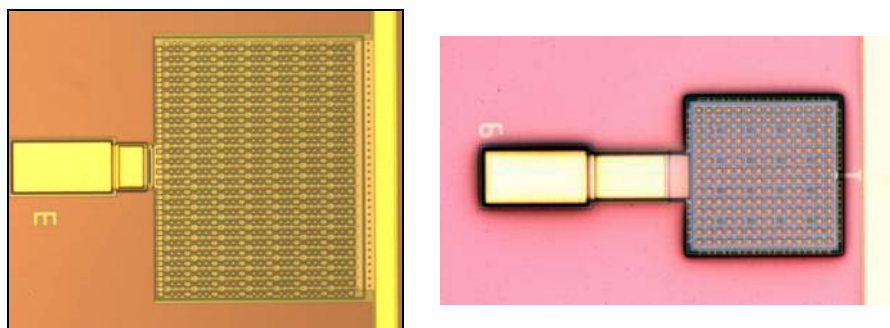
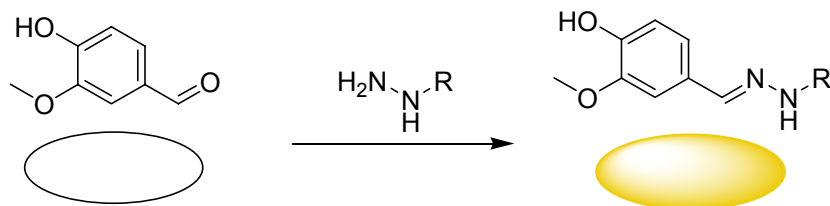


Figure 1. Architecture of Seacoast Science’s IDT (left) and parallel-plate (right) sensor platform.

The IDT fingers are 400 microns long, $3.5\mu\text{m}$ wide, and have 25 alternating sense and drive electrode pairs (each beam separated by $3.5\mu\text{m}$) in parallel supported by $2\mu\text{m}$ tall insulating posts above the lower substrate. The parallel-plate structure is made of two stacked electrodes, $285\mu\text{m}$ on a side, separated by $0.75\mu\text{m}$.

Hydrazine Detection

Other methods for the detection of Hydrazine (Hz), Monomethyl hydrazine (MMH), and 1,1-dimethylhydrazine (UDMH) have been reported in scientific literature and patent literature. One ubiquitous reaction used for the detection of these species is the reaction of hydrazine with aromatic aldehydes (9). This reaction was used in the design of a colorimetric detection of hydrazine in a badge format (Scheme 1) (10).



Scheme 1. Reaction of hydrazine with 4-methoxybenzaldehyde for colorimetric detection system.

Others have used this reactivity in the design of optical sensor based on sol-gel chemistry (11), and has been used to derivatize hydrazine prior to detection by gas chromatography (12) or ion mobility spectroscopy (13). Direct detection of hydrazines has also been reported with an iridium based thermal sensor (14) or a surface acoustic wave (SAW) device (15). Various electrochemical detection schemes have been reported using a functionalized polysilsesquioxane film (16), polyaniline derivatives (17), poly(hexylthiophene) (18), polypyrrole (19.), nickel dithiolene complexes (20), cobalt phthalocyanines (21) modified carbon electrodes (22) or polymer coated electrodes (23). There is also a commercially available hydrazine detector that uses a wet chemical cell for the detection of atmospheric hydrazine (Interscan Corporation. Specifications: Weight: 22 lb (10.0 kg) Dimensions: 22" H x 18" W x 8.5" D <http://www.gasdetection.com>). The techniques listed above suffer from size, power, or other operational limitations that our MEMS based chemocapacitors sensors will address (*vide infra*).

Experimental

Two micromachined chemicapacitor designs are used in this study; a parallel-plate structure and elevated interdigitated (IDT) electrode architecture (*vide supra*). The sensor chips were fabricated using the Multi-User MEMS Process at MEMSCAP, Inc., Durham, NC. The detection and control electronics along with the test system used to obtain the present measurements on all sensor types have been reported previously (7, 8, 24). The chips measure 5mm×2mm and contained ten chemicapacitors with either IDT or parallel-plate geometries. Each capacitor is coated or filled with a different polymer or other dielectric material using an inkjet system (8). Readout electronics have been described in detail (8, 25). Chemoselective polymers and materials were purchased, provided by a collaborator, or synthesized in house (26, 27). Tests were performed in a custom-built vapor test system designed to accurately deliver calculated quantities of analyte based upon its reported vapor pressure and coefficients (28) using the Antoine Equation (29). Hydrazine (Hz), Monomethyl hydrazine (MMH), and 1,1-dimethylhydrazine (UDMH) were purchased from Sigma-Aldrich Chemical Company (St.

Louis, MO) and used as received. NO₂ (5000 ppm in N₂) was purchased from Scott Specialty Gases (Plumsteadville, PA).

Results and Discussion

Selection of the polymers for detection of hypergolic compounds was based upon the predicted binding properties of materials (i. e. H-bonding, polarity, acidity, oxidation state) (Figure 2).

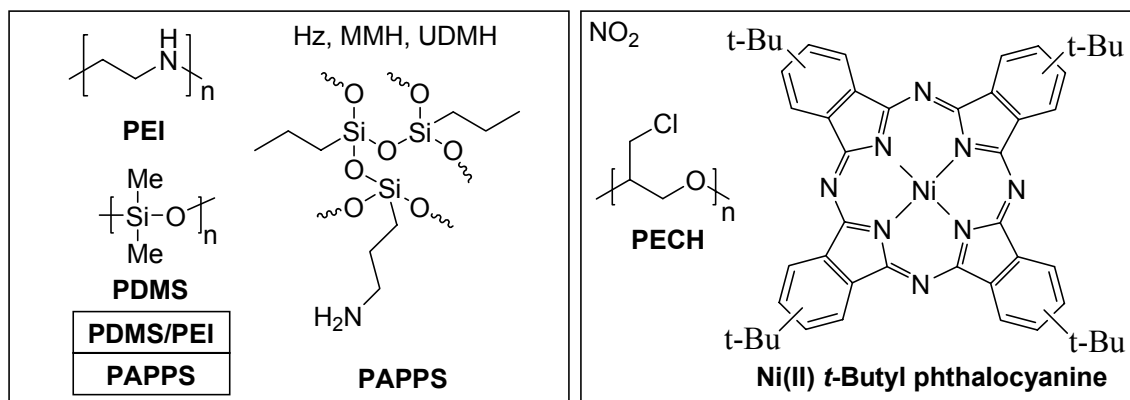


Figure 2. Optimal sensor materials used for the detection of hypergolic compounds. (PDMS: poly(dimethylsiloxane), PEI: poly(ethyleneimine): PAPPS: propylamino-propylpolysilsesquioxane; PECH: poly(epichlorohydrin))

The presence of water was necessary for detection of hydrazines as illustrated in the response of the PEI/PDMS/PAPPS composite sensor to MMH (Figure 3).

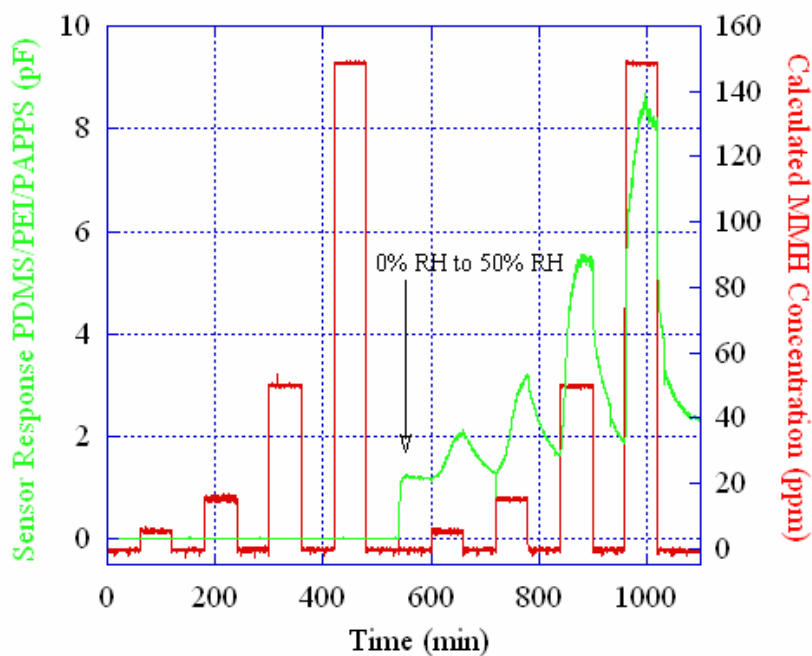


Figure 3. Sensor Response of PDMS/PEI/PAPPS to MMH under variable humidity (T = 25°C)

With the dry carrier gas, no signal is observed even at high MMH concentration (~ 1650 ppm); increasing the humidity to 50%, a strong signal is observed even the lowest concentration (~If the material consisted only of silica, a proton transfer would be thermodynamically favored with the pK_a of the silanol ~4.5 and the pK_a of the hydrazinium ion ~ 8 (30). However, with the composite nature of the sensor, it seems unlikely that bare silanol groups are on the sensor surface. Furthermore, the PAPPs material and the PEI contain primary amines that would also participate in any proton transfer. The dependence of the signal upon the humidity is also somewhat puzzling. One explanation is that with dry carrier gas (compressed air), all the hydrazines ‘stick’ to the surface of the test system and the water simply acts as a carrier for the hydrophilic fuels. Another hypothesis is that the water ‘activates’ the sensor surface towards the detection of the unsubstituted and substituted hydrazines. Regardless of the mechanism involved, the dependence of the signal upon the presence of water will be an advantage for applications of hydrazine detection in humid environments (i. e. shipboard).

Nitrogen tetroxide (NTO) was selected as a representative oxidizing agent. Due to the health and safety hazard of NTO we took advantage of the equilibration of NTO in air (31).



The chemoselective materials were exposed to varying concentrations of NO_2 (diluted in nitrogen). Of the materials tested, poly(epichlorohydrin) (PECH) and a nickel centered substituted phthalocyanine (32) were most sensitive (Figure 4).

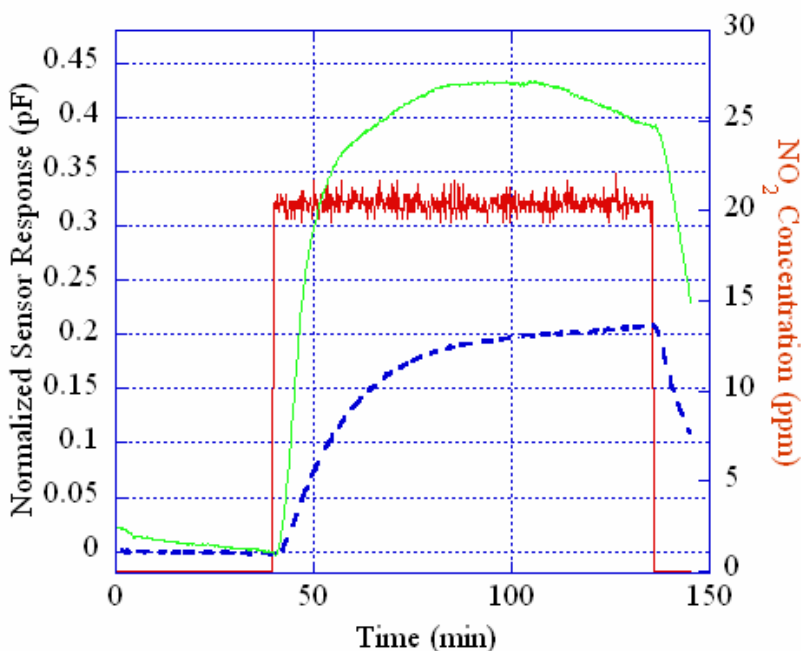


Figure 4. Sensor Response of PECH (dashed line) and Ni (II) phthalocyanine (solid line) to NO_2 (0% RH, T = 25°C).

The high sensitivity of PECH to NO_2 was rather unexpected and must be due to a dipole-dipole or Van der Waals interaction. A similar sensitivity of PECH to nitroalkanes and

nitroaromatics was recently reported (33). For the nickel-phthalocyanine species, a possible explanation involves the oxidation of the Ni(II) to Ni(III). This hypothesis was supported by observation of an irreversible response of the sensor upon exposure to higher concentrations NO₂.

From the sensor responses the limits of detection were calculated (8) for the hydrazine species and NO₂ (Table I).

TABLE I. Detector results and limits of detection for hypergolic compounds.

Analyte	Optimal Material	Limit of Detection (ppm)
Hydrazine	PDMS/PEI/PAPPs	10.2
Methyl Hydrazine	PDMS/PEI/PAPPs	0.26
1,1-dimethyl hydrazine	PDMS/PEI/PAPPs	0.27
Nitrogen dioxide	Ni(II) <i>t</i> -butyl phthalocyanine	0.14
Nitrogen dioxide	PECH	0.30

Conclusions

A first generation hypergolic fuel sensor array was developed using a chemicapacitive sensor array coated or filled with suitable materials. A composite sensor material with a polysilsesquioxane base and polymer (PEI/PDMS) coating was the optimal material for the detection of Hz, MMH, and UDMH. For NO₂ both PECH and a Ni centered substituted phthalocyanine complex gave sub-ppm detection at ambient temperature. The hydrazines were detected at levels far below the lower explosive limit (~25000 ppm) and below the IDLH (20 ppm) for MMH. This sensor array can be incorporated into a three-tier sensor system for the KEI and may provide solutions for industrial and safety monitoring of NO₂ as well as substituted and unsubstituted hydrazines.

Acknowledgments

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