

Chemicapacitive microsensors for detection of explosives and TICs

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ABSTRACT

Seacoast Science develops chemical sensors that use polymer-coated micromachined capacitors to measure the dielectric permittivity of an array of selectively absorbing materials. We present recent results demonstrating the sensor technology's capability to detect components in explosives and toxic industrial chemicals.

These target chemicals are detected with functionalized polymers or network materials, chosen for their ability to adsorb chemicals. When exposed to vapors or gases, the permittivity of these sorbent materials changes depending on the strength of the vapor-sorbent interaction. Sensor arrays made of ten microcapacitors on a single chip have been previously shown to detect vapors of organic compounds (chemical warfare agents, industrial solvents, fuels) and inorganic gases (SO₂, CO₂, NO₂).

Two silicon microcapacitor structures were used, one with parallel electrode plates and the other with interdigitated "finger-like" electrodes. The parallel-plates were approximately 300 μm wide and separated by 750 nm. The interdigitated electrodes were approximately 400 μm long and were elevated above the substrate to provide faster vapor access. Eight to sixteen of these capacitors are fabricated on chips that are 5 x 2 mm and are packaged in less than 50 cm³ with supporting electronics and batteries, all weighing less than 500 grams. The capacitors can be individually coated with different materials creating a small electronic nose that produces different selectivity patterns in response to different chemicals. The resulting system's compact size, low-power consumption and low manufacturing costs make the technology ideal for integration into various systems for numerous applications.

Keywords: Chemicapacitor, microsensor, chemical detector, explosives, toxic industrial chemicals, capacitive detection, dielectric constant, polymers

1. INTRODUCTION

Toxic industrial chemicals, improvised explosive devices, and chemical warfare agents are growing threats to warfighters as well as civilians. Recent bombings in the London subway system underscore this threat. Most current sensor technologies have not yet been proven to detect these threats at sufficient concentrations, and those that do, require too much power, are too large, or are too expensive to be widely distributed. Protecting an entire subway train requires multiple sensor nodes; an entire mass transit system presents an expensive problem. New sensor technologies are required to bridge the gap between small man-portable systems and large, expensive high sensitivity systems. Novel solutions could be stand-alone or deployed in tandem with other detectors to increase sensitivity or specificity and to fill in gaps in existing protection networks.

In addition to defensive and homeland security applications, industrial applications are also significant considering that over 2 million metric tons of industrial explosives are sold annually in the United States, for uses such as mining, quarrying and construction¹. Other applications of nitroorganic-compounds include the manufacture of polyurethane and gun powder (e.g. from dinitrotoluene), aniline (e.g. from nitrobenzene), solvents, inks, paints (e.g. nitropropane), and fertilizers.² Sensors are required to secure these toxic industrial chemicals from potential terrorists and for everyday industrial operations such as monitoring storage, transport, process control, and waste management.

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Chemical capacitors have been used primarily to detect humidity^{3,4}; however, recently they have been reported to detect many different compounds, including solvents, common volatile organic compounds (VOCs)^{5,6,7}, toxic industrial chemicals⁸, chemical warfare agents⁸, and inorganic gases such as carbon dioxide⁹ and ammonia¹⁰. The specifics of the detection mechanisms have been studied previously^{5,7} and have been found to rely on a combination of interactions arising from vapor sorption, including polymer swelling and other changes in the morphology.

Seacoast Science, Inc. is developing a sensor technology using a single-chip array of polymer filled microcapacitors. The small (5 x 2 mm) chips and low-power electronics provide a simple detector system that can be manufactured for approximately \$1000 in prototype quantities. Capacitance measurement systems, such as those for MEMS pressure sensors and accelerometers are commonly produced for less than \$100, providing support for further cost reduction. The system can be integrated with wired or wireless communications, providing a distributed network of sensors. In this paper we present recent results from chemical exposure tests with nitro-aromatics and nitro-alkanes to determine the viability of using chemically capacitive technologies to detect explosives and similar toxic industrial chemicals.

2. EXPERIMENTAL

Seacoast Science's chemically capacitive sensors and readout electronics have been described in detail^{7,8}. 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. Two chemically capacitive structures were evaluated in the present study (Figure set 1).

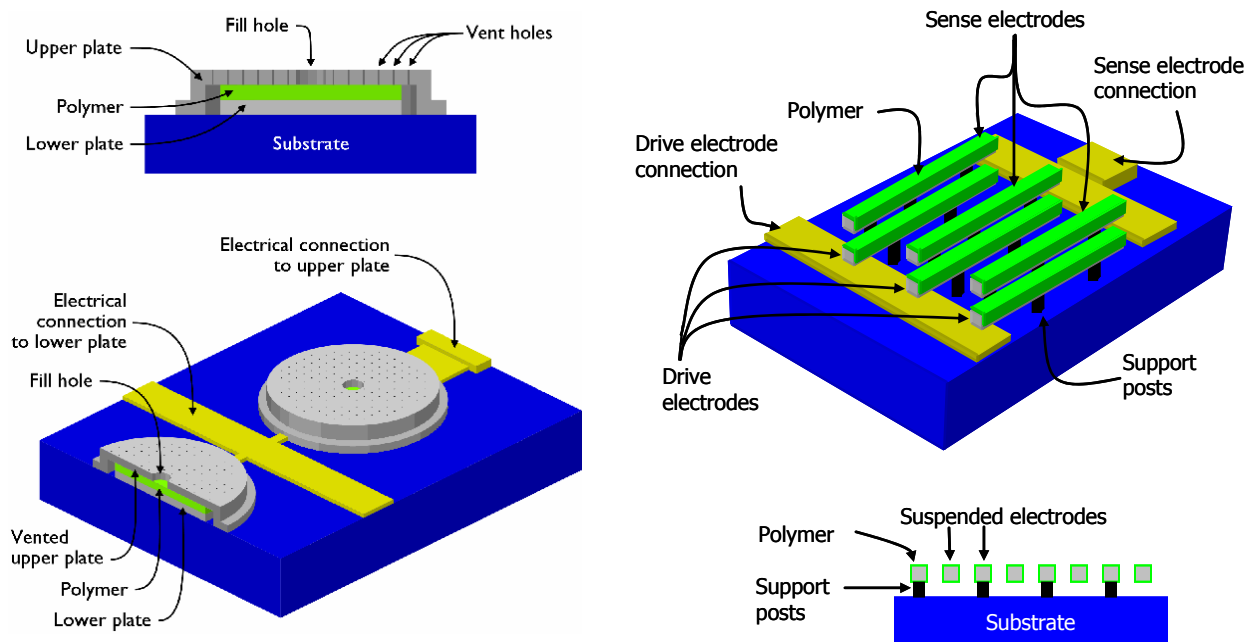


Figure 1a. Cross-sectional diagrams of the parallel-plate sensor element.

Figure 1b. Cross-sectional diagram of the elevated IDT structure.

The two structures can be fabricated simultaneously using the Multi-User MEMS Process (MUMPS) at MEMSCAP (Durham, NC) and can be made in any combination. The typical parallel-plate (PP) capacitor is circular or square, approximately 300 to 400 μm wide, and has a perforated top plate suspended over a solid bottom plate, with a 0.75 μm gap between the plates. In the parallel-plate structure, all of the externally generated electric field passes between the top and bottom plate, with very little effect from the edges. The interdigital transducers (IDT) are approximately 400 μm long and 3.5 μm wide, and have 25 alternating sense and drive electrode pairs (each beam separated by 3.5 μm) in parallel supported by 2 μm tall insulating posts above the lower substrate. This structure is similar to conventional interdigitated capacitive sensors³ in that the electric field can pass between the alternating electrodes and the air or substrate above and below the sensor.

The sensors are either coated (IDT) or filled (parallel-plate) with polymeric or network materials using an inkjet device.⁸ The polymers are dissolved in an appropriate solvent such as water, acetone, chloroform, or toluene at a ratio ($\leq 1\%$ wt/wt). For the parallel-plate design, the capacitors are filled by depositing the dissolved material through the porous top plate. For the IDT structure, much less material is used and the material is coated onto the beams and top surface of the substrate. Capillary forces keep the polymers between the parallel-plates, while surface tension and adhesion are relied upon for the IDTs. This makes the parallel-plate devices a more stable device in general, however due to a shorter diffusion path; the IDT devices respond and reach equilibrium with the environment much faster than the parallel-plate sensor elements⁸.

Polymers are applied to the sensors with an inkjet head similar to that used in printers. The head, which is mounted on a translation stage, has a 30 or 80 μm diameter nozzle that expels droplets of a polymer solution (Figure 2). Each drop is typically a few tens of picoliters in volume and 30-100 μm in diameter. When a coated sensor is exposed to a VOC, it passes through the perforations in the top plate and absorbs into the polymer, changing the permittivity or dielectric constant of the capacitor and therefore its capacitance.

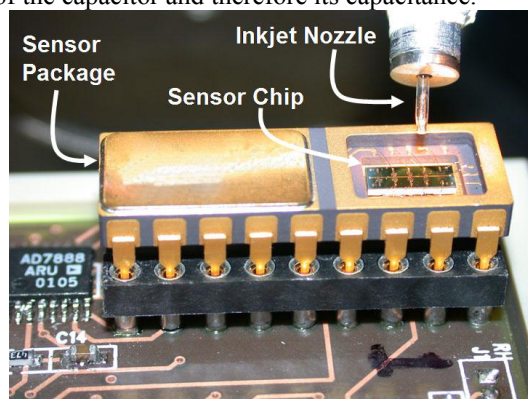


Figure 2. Close up of the inkjetting process. Coating is performed while all of the capacitors on the chip are measured in real-time, thus ensuring quality control. Sensor chip is wirebonded in the open cavity of a dual-cavity ceramic DIP.

Pattern recognition algorithms in conjunction with a multiple-sensor array have been shown to mitigate cross-sensitivities.^{11,12,13} Polymers are selected^{14,15,16,17} based on their ability to form stronger reversible chemical bonds (hydrogen bonds, π -stacking, van der Waals interactions, and dipole-dipole interactions) with the analyte than with interferents. The amount of VOC that absorbs into the polymer depends on chemical and physical properties of the polymer. The side chain groups can have a great influence on relative sensitivities to certain chemicals. By taking advantage of these specific chemical interactions and by comparing the responses of several capacitors, each filled with a different polymer; it is possible to distinguish different VOCs from each other.¹⁸

The capacitance measurement is accomplished by an application-specific integrated circuit (ASIC) that outputs a voltage proportional to each capacitance.^{6,7,8} The sensor and readout chips are therefore packaged together in a hybrid ceramic dual in-line package (DIP) (Figure 2). The readout chip is placed in a hermetically-sealed cavity; whereas the sensor chip is in a cavity that is open to the environment (after coating, a fine-pitch screen backed by a PTFE filter is used to protect it from dust). The ceramic DIP is mounted on the system “motherboard”, which contains a microcontroller, output devices, and RS232 transceiver for data collection. The measured voltage is related to the sensor’s capacitance by Equation 1:

$$\Delta C = \Delta C_{reference} \left(\frac{\Delta V_{measured}}{V_{osc}} \right) \quad (1)$$

where ΔC is the measured change in capacitance, $\Delta C_{reference}$ is a reference capacitor (either 0.5 or 1 pF) within the ASIC, V_{osc} is the amplitude of the drive waveform applied to the sensor (typically between 0.05 to 1 Volt), and $\Delta V_{measured}$ is the change in output voltage measured during chemical exposure minus the voltage measured before chemical exposure. For all of the data presented in this paper, $\Delta C_{reference}$ and V_{osc} were held constant during each experiment. More details can be found in previous publications^{6,7}.

Table 1. Polymers for Chemicapacitor Sensors

Polymer	Characteristics
Poly(ethylene-co-vinyl acetate) (PEVA)	Low crystallinity, low polarity
Polyepichlorohydrin (PECH)	Low polarity
Siloxane fluoroalcohol (SXFA)	H-Bond acid, high polarity
Cyanopropyl methyl phenylmethyl silicone (OV225)	H-Bond basic, Polar
Poly(cyanopropyl siloxane) (OV-275)	H-Bond basic, high polarity
Polyethylene oxide (PEO)	Crystalline, high polarity

The polymers in Table 1 are listed in order of increasing dielectric constant, with PEVA having the lowest permittivity and PEO the highest.⁷ In this study, we are investigating polymer-based chemicapacitors to detect targets such as explosives, simulants and taggants, and to identify which polymer functionalities can be used to identify these vapors. Target chemicals include 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), ortho-mononitrotoluene (*o*-NT), nitrobenzene (NB), 2,3-dimethyl 2,3-dinitrobutane (DMDNB), 1-nitropropane (NP); and several common volatile organic compounds (VOC) such as acetone, octane, allyl alcohol, and ethanol. Some of these targets are used as taggants in commercial explosives, such as mononitrotoluene¹⁹ or DMDNB required in PETN sheets²⁰. While others are simulants, are considered high explosives¹⁹, or are major signature chemicals, such as dinitrotoluene in TNT (trinitrotoluene)²¹. Vapor pressures were estimated from or found in the literature or material safety data sheets (MSDS).

Vapors were delivered by either bubbling air through temperature controlled liquid or passing air over the headspace of solid samples, and then diluting to the appropriate concentrations. The diluted vapor is passed over the sensors in a temperature controlled silco-coated stainless steel chamber. All flows were controlled with electronic mass flow controllers, and a humidity sensor (Hycal from Honeywell, inc.) was used inside the test chamber to monitor the ambient humidity. Glass-fritted bubblers were used to contain the analytes, and all of the wetted lines were heated to at least 50°C to reduce the overall equilibration time of the test system.

3. RESULTS AND DISCUSSION

Previous studies of these sensors have shown that chemicapacitors have sensitivity levels to volatile organic compounds⁷ that are comparable to that of other polymer-based VOC sensors, with sufficient sensitivity to detect common industrial solvents below 100 parts-per-million (ppm)⁷. The chemicapacitor as a sensor platform has proven to be compatible with a wide range of chemoselective coatings, including materials synthesized *in situ*, expanding the range of detection to include other classes of chemicals including many toxic industrial chemicals⁸ and nerve agents at concentrations below 10 parts-per-billion (ppb)⁸. Data are presented as raw voltage as measured from the sensor, or as change in voltage from baseline conditions. Noise is typically between 0.2 and 1 mV.

Figure 3 shows the response of two coated chemicapacitors to acetone, ethanol and octane vapors. This is a sample of the response profiles and selectivity trends

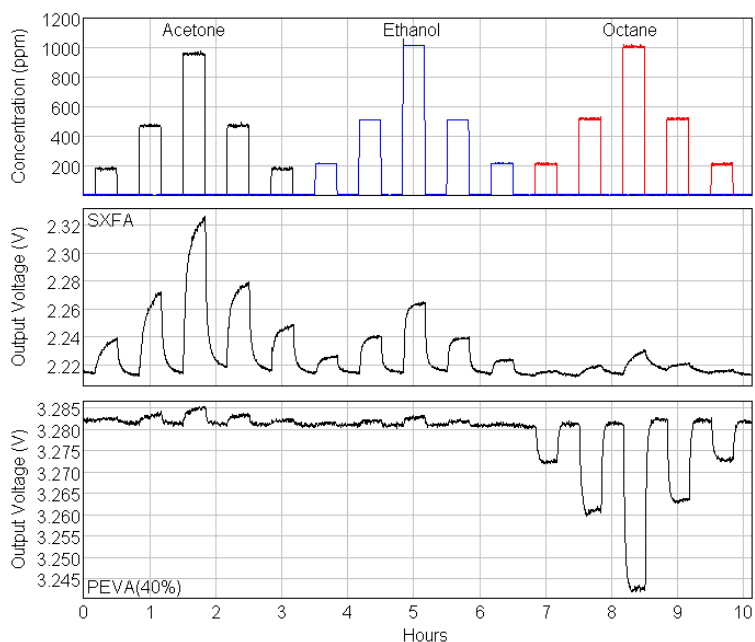


Figure 3. Response of PEVA and SXFA to acetone, ethanol and octane at 25°C and a background relative humidity of 20%.

observed from the sensors. PEVA, coated on a parallel-plate sensor, shows a decrease in capacitance from octane, with little response to acetone. This type of behavior was previously reported, and was attributed to polymer swelling dominating the overall permittivity change^{5,7}. SXFA, coated on an IDT device, shows an increase in capacitance to all three chemicals, but a higher selectivity towards acetone versus octane. Figure 4 shows the response from several low-concentration vapor exposures of allyl alcohol to the same SXFA coated sensor in Figure 3.

Figure 5 shows relative responses of several coated sensors to common VOCs and water vapor. The VOC concentration was 200 ppm for each and the water vapor concentration was 6250 ppm or 20% relative humidity at 25°C.

In contrast to the VOC test results, the OV225 coated sensors exhibit a high affinity for

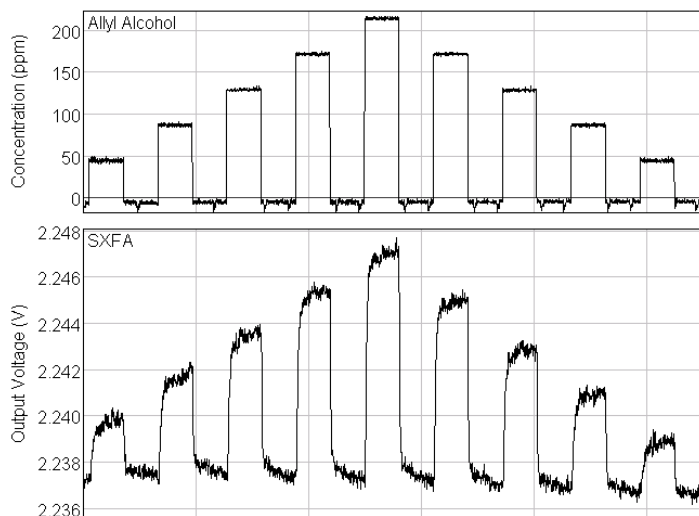


Figure 4. SXFA coated sensor responding to allyl alcohol at 35°C and 0% relative humidity.

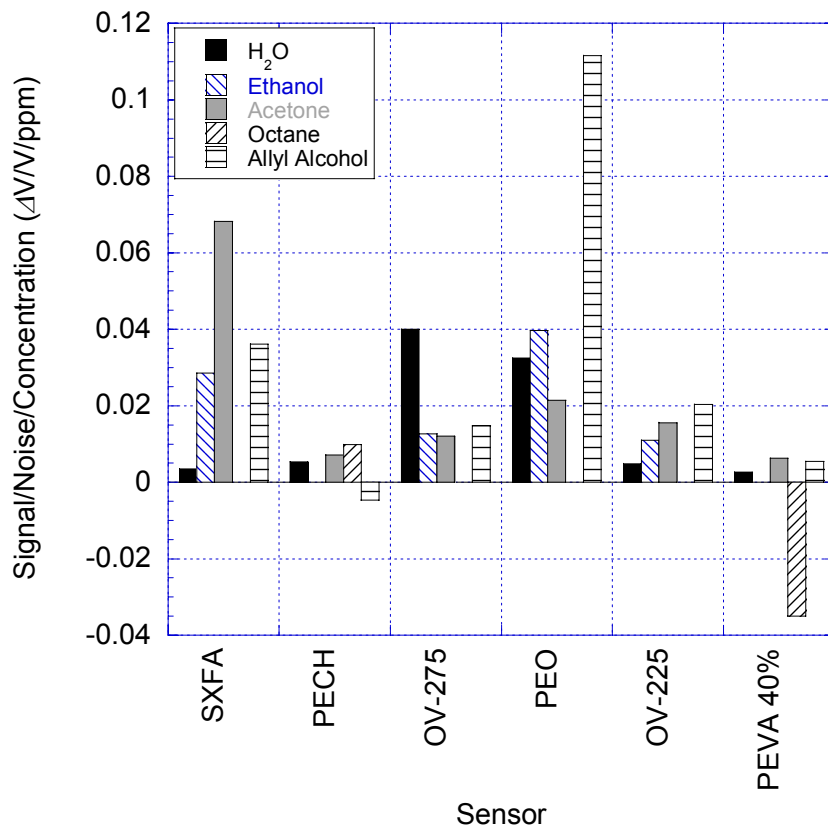


Figure 5. Signal to noise response normalized to ppm concentration of analyte.

the nitro-containing compounds, in general, and the nitroaromatic compounds specifically²². Figure 6 contains a plot of responses from an OV225 filled chemicapacitor exposed to several vapors at different temperatures. The sensor shows ppm level sensitivity to 1-nitropropane exposures over a range of temperatures and at a range of concentrations, while both 2,4-DNT and DMDNB can be detected at much lower concentrations.

Lower concentrations are detectable at lower temperatures owing to the fact that the vapors partition into the polymer phase better at lower temperatures. However the vapors diffuse faster through the polymer and environment at higher temperatures, resulting in faster equilibrium and therefore faster response times. OV225, a siloxane with both aromatic and cyano-alkane pendant groups, has a higher affinity for the nitroaromatic compounds compared to the nitropropane. Using OV225, the explosives taggant DMDNB was detected at approximately 27 ppb at 25°C, while 2,4-DNT was detected at 21 ppb at 20°C.

Similarly, all of the sensors show strong dependencies on temperature, i.e. higher sensitivities at lower temperatures when exposed to nitrotoluene (Figure 7). Of these, PECH, OV225, and SXFA show the highest sensitivity to the nitroaromatic compound. We hypothesize that the nitrotoluene acts as a hydrogen-bond base and interacts reversibly with the strong hydrogen bond acid group (perfluoroisopropanol) in SXFA. However, the sensitivity of PECH to *o*-nitrotoluene must be due either to dipole-dipole or Van-der Waals forces.

Figure 8 shows the response of several polymer filled chemicapacitors to 2,6-DNT vapors at 20°C in a background of 60% relative humidity. PECH provides a variation in selectivity not seen in

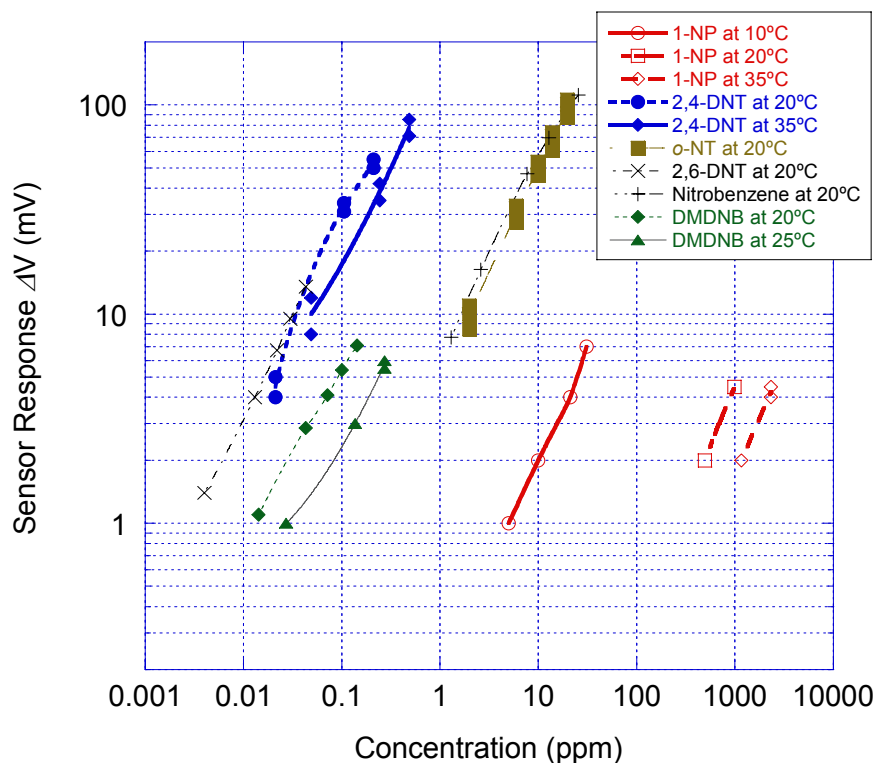


Figure 6. Response curves of a parallel-plate chemicapacitor filled with OV225.

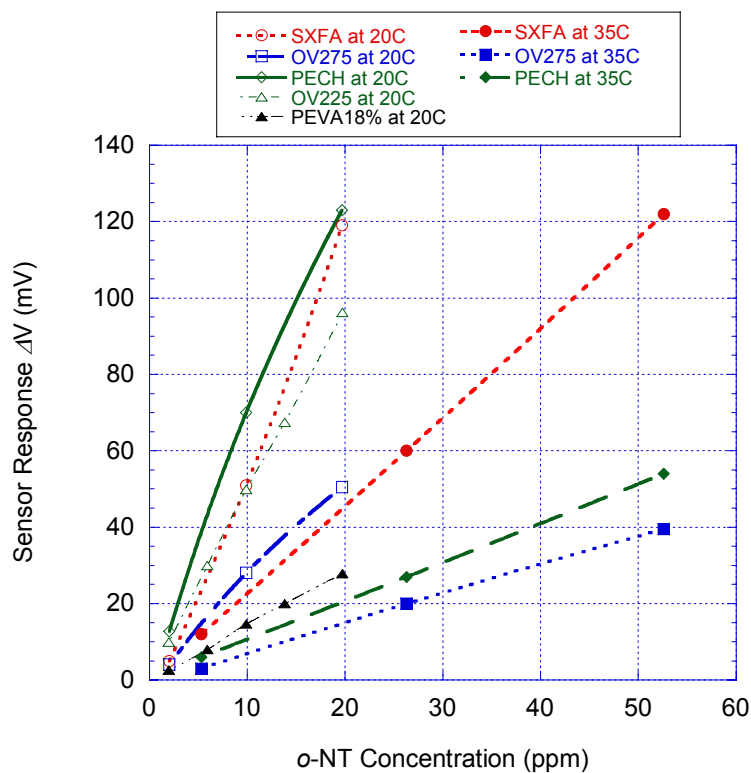


Figure 7. Response of chemicapacitors to *o*-nitrotoluene vapors at 20° and 35°C over a range of concentrations. The background humidity was 0%.

the other sensors, namely a decreasing sensor capacitance, i.e. the permittivity of the sensors' dielectric material decreases upon exposure. In response to common solvents such as toluene or benzene this type of behavior can be attributed to swelling in the polymer, however with such low concentrations and the fact that 2,4-DNT does not appear to behave the same way with PECH, it is hypothesized that there is a specific interaction causing the decrease in capacitance.

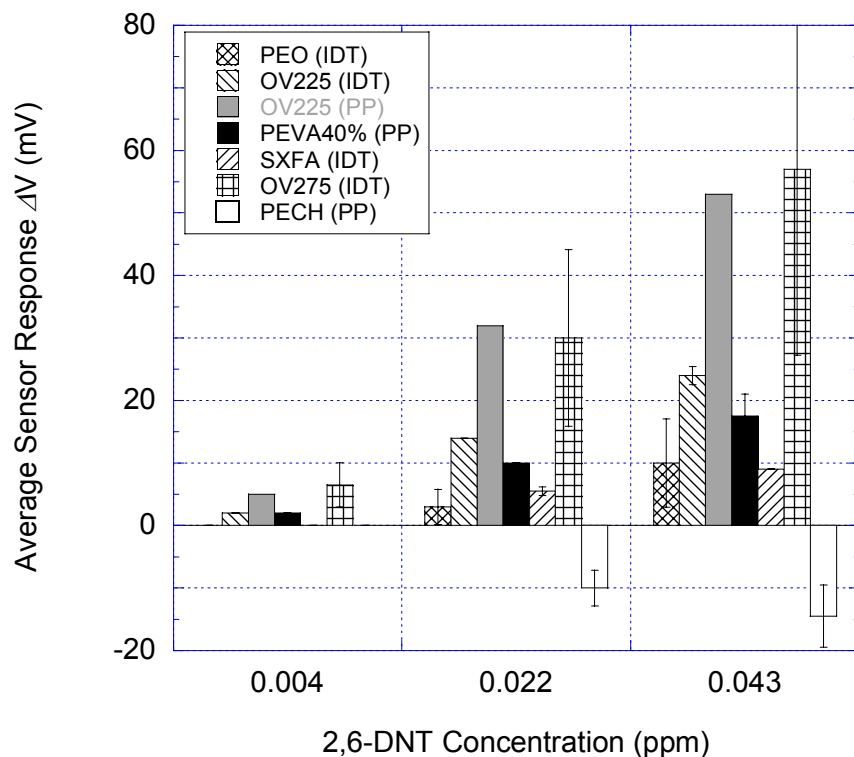


Figure 8. Response of several polymer filled chemicapacitors to 2,6-DNT vapor at 20°C and a background humidity of 60%. Sensors were coated and tested in pairs, and the data averaged, except for OV225, which has 1 parallel plate sensor coated and 2 IDTs. Error bars represent the standard deviation of the measured responses.

The OV225 coated IDTs showed lower sensitivity to the 2,6-DNT vapors compared to the parallel-plate coated sensor, however the difference is difficult to quantify since the IDTs are dependant upon the location and thickness of the coatings while the parallel-plate sensors are independent of topological effects due to the fixed volume.

Figure 9 shows OV225 and PECH responses to the explosives taggant DMDNB at two temperatures and under dry conditions. In the figure the sensors (two with each polymer) are parallel-plate structures and the responses show a similar dependence with temperature. The Figure 10 shows that there is some variation in sensitivity with the presence of relative humidity. Each point is referenced to zero concentration of 2,6-DNT at each relative humidity level. Water vapor appears to compete with the DNT, reducing the sensors' sensitivity compared to dry conditions.

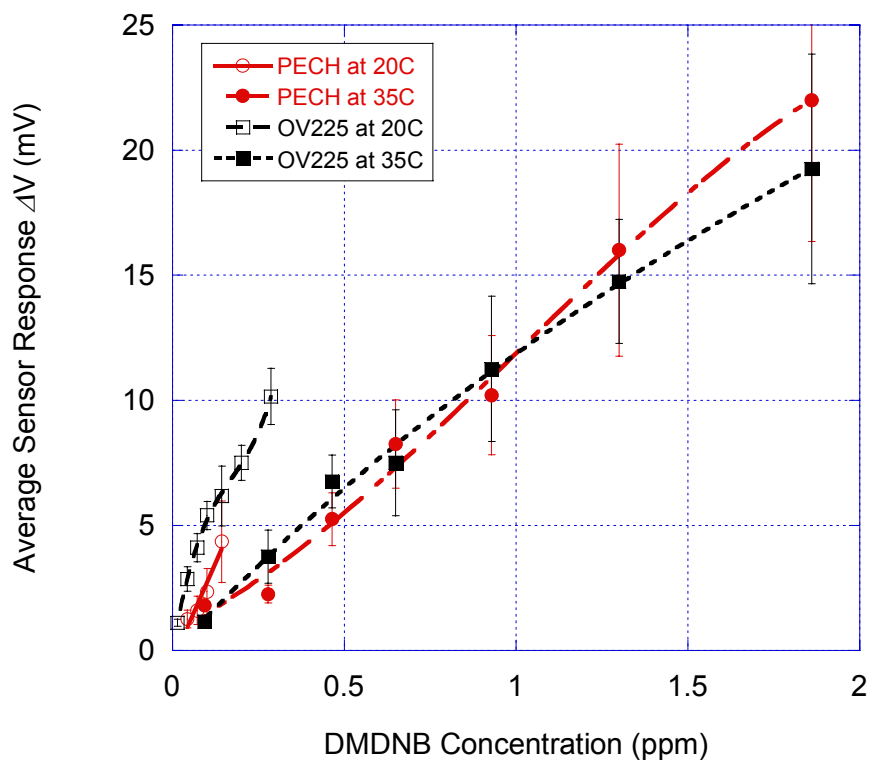


Figure 9. Response of a OV225 and PECH filled parallel-plate structures to DMDNB exposures at two temperatures. Data points represent averaged measurements from two sensors of made from each polymer. Error bars represent the standard deviation of the measured responses.

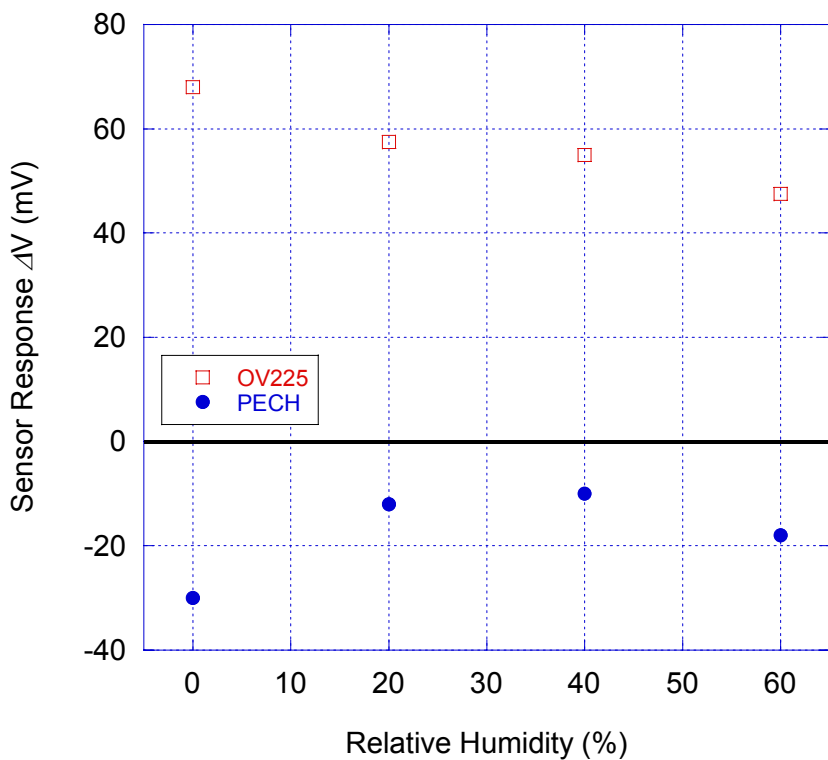


Figure 10. Response of an OV225 filled chemicapacitor and a PECH filled chemicapacitor to 43 parts-per-billion of 2,6-DNT at 20°C at four relative humidity levels.

Table 2 shows the estimated limits of detection from the tests of the explosive simulants and taggants near or at room temperature. The theoretical limits of detection (LOD) have been calculated using a signal to noise limit of 3:1.

Table 2. Theoretical limits of detection for the nitro-compound vapors.

Analyte	LOD (ppm)	Polymer/Sensor ^a	Temperature (°C)
DMDNB	0.02	OV225	25
	0.06	PECH	25
<i>o</i> -Nitrotoluene	0.5	OV225	20
	0.4	PECH	20
2,6-DNT	0.001	OV225	20
	0.002	PECH	20
2,4-DNT	0.01	OV225	20
	0.03	PECH	20
1-Nitropropane	10	OV225	25
	22	SXFA	25
Nitrobenzene	0.4	OV225	20
	0.1	OV225	10

^a parallel plate architecture used in all sensors except SXFA

Establishing an equilibrated vapor stream of low-vapor pressure chemicals can take several hours, therefore some of these chemicals were exposed for several hours before sensor equilibrium was established. The limits of detection are generally higher (poorer) at higher temperatures owing to the shifted vapor-solid equilibrium, as shown by the LOD values for nitrobenzene at 20° and 10°C. In general, the low-vapor pressure compounds (e.g. DNT) could be detected at concentrations several orders of magnitude lower than the higher vapor pressure compounds (e.g. nitropropane).

4. SUMMARY AND CONCLUSIONS

We have established the viability of Seacoast Science's capacitive sensors by demonstrating detection of high explosives, taggants, and simulants for explosives. While sensor responses were generally faster with interdigitated architecture chemicapacitors, the highest sensitivities were found with the parallel-plate design. We have shown that micromachined, parallel-plate capacitors can be filled with polymers and used to detect both vapors from explosives such as 2,4-DNT and 2,6-DNT, and to detect the common taggant DMDNB.

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