



Chemicapacitive microsensors for volatile organic compound detection

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Received 23 December 2002; received in revised form 11 July 2003; accepted 22 July 2003

Abstract

A low-cost, low-power volatile organic compound (VOC) sensor has been constructed from an array of micromachined parallel-plate capacitors. The sensor has demonstrated detection of many VOCs well below the lower explosive limits and could be used in industrial leak monitoring applications or for homeland defense. In place of a standard dielectric, the individual capacitors were filled with selectively absorbing polymers. Absorption of a target vapor alters the permittivity of the polymers and thereby changes the capacitance of the elements in the array. A variety of polymers have been used, including polyethylene-co-vinylacetate, which was sensitive to nonpolar hydrocarbons, and siloxane-fluoro alcohol, which was highly sensitive to polar VOCs and chemical warfare agent simulants. The response magnitude for each element depends on a combination of different phenomenon such as the dielectric constant of the analyte and polymer swelling. The measured sensitivity of the sensor to most VOCs was found to be in the low parts per million (ppm) range. The response magnitude from one capacitor to the next is reproducible to within 3.2% at 20 °C. The sensor typically responded within a second but frequently required 5–10 min to reach equilibrium. Response times could likely be substantially improved with an optimized capacitor structure that contains a decreased gap between the plates and provisions for more rapid vapor exchange.

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Keywords: VOC; MEMS; Capacitance; Permittivity; Polymer; Sensor; Array; Dielectric

1. Introduction

Volatile organic compounds (VOCs) are widely used in industry and can present serious medical, environmental, and explosion dangers. VOC sensors are therefore commonly used to monitor oil-drilling platforms, fuel storage tanks, air pollution sources, and other locations where VOC leaks may occur. VOC sensors are also useful in civil defense and military applications, because many chemical warfare agents and explosives can be detected with VOC sensor technology.

The ultimate goal of the present work is to produce distributed wireless sensor networks containing numerous battery-operated, low-cost, low-maintenance VOC point

sensors. Such networks would provide faster response times and lower operating costs than manually conducted surveys with handheld sensors. To this end we are developing sensors based on selectively absorbing polymers. The selectivity of these polymers results from functional groups that interact weakly with certain target analytes, imparting some degree of preferred interaction. Each element in the sensor array can contain a different polymer, and the collective information from the responses of all elements of the array is used to identify an unknown analyte. Our polymer-based sensors require relatively simple, low-power detection hardware and can operate unheated at ambient temperatures.

1.1. Polymer-based VOC sensors

The amount of VOC absorbed into a functionalized polymer depends not only on the ambient concentration of the VOC, but also on the chemical properties of the VOC and polymer. The specific chemical properties that affect absorption are reflected in solubility-prediction systems such as the Hansen solubility parameters [1,2] or the linear solvation

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56 energy relationship (LSER) [1,3]. Hansen solubility param- 112
57 eters are empirically determined parameters that indicate the 113
58 dispersion, dipolar, and hydrogen-bonding strength of nu- 114
59 merous organic compounds; compounds having similar sol- 115
60 ubility parameters are typically highly soluble [4,5]. LSER 116
61 relates the chemical properties of materials, combining fac- 117
62 tors such as polarizability, dipolarity, hydrogen bond-acidity, 118
63 and hydrogen bond-basicity, to determine the gas–liquid par- 119
64 tition coefficient (K_p). 120

65 In the arena of microfabricated chemical sensors, a num- 121
66 ber of groups have developed VOC sensors based on poly- 122
67 mers that selectively absorb the VOC of interest. These sen- 123
68 sors measure one or more polymer properties that change 124
69 when a VOC is absorbed. For example, researchers have 125
70 used resistive sensors [4–7] and cantilever stress sensors 126
71 [8–17] to measure swelling of the polymer; resonating can- 127
72 tilevers, surface acoustic wave (SAW) devices [3,18–20], 128
73 and flexural plate wave (FPW) sensors [21] to measure mass 129
74 and viscoelasticity changes; and capacitive sensors [22–29] 130
75 to measure changes in polymer permittivity. 131

76 Surface plasmon resonance (SPR) sensors use phonons 132
77 created from light reflected off of thin metal surfaces, which 133
78 can be coated to provide selectivity enhancements similar 134
79 to other polymer-based sensors [30]. Polymer-based sen- 135
80 sors that measure changes in a coating’s index of refraction 136
81 or fluorescence have also been used to detect VOCs as 137
82 well as other chemical and biochemical compounds [31,32]. 138
83 These sensors generally operate on the same solubility-based 139
84 principles as the microfabricated devices, by measuring the 140
85 changes in the properties of the coatings, however, they 141
86 may also be sensitive to the optical properties of the target 142
87 analyte. 143

88 Generally, polymer-based sensors can be used to de- 144
89 tect most volatile and semi-volatile organic compounds. 145
90 Highly volatile chemicals, those that are gases at room 146
91 temperature and pressure, such as methane, are difficult to 147
92 detect since they do not absorb into polymers well, while 148
93 low-volatility, solid compounds such as some explosives 149
94 produce insufficient vapor-phase material for detection. 150
95 Polymer-based sensors can detect industrial solvents, liquid 151
96 fuels, many chemical warfare agents, and certain volatile 152
97 compounds present in commercial explosives. In addition, 153
98 polymer-based sensors have been used to detect several 154
99 non-VOC compounds, particularly water vapor [23–27] and 155
100 ammonia [28]. 156

101 Although such sensors have proven successful in a num- 157
102 ber of applications, various difficulties have prevented the 158
103 development of low-cost, low-maintenance VOC sensors. 159
104 Variations in polymer composition or nonuniform polymer 160
105 films can cause poor unit-to-unit reproducibility, necessitat- 161
106 ing costly calibration of each unit. In addition, sensor output 162
107 can drift due to chemical interactions of the polymer with 163
108 the environment, creating a need for frequent recalibration 164
109 or for periodic rezeroing with automated exposures to clean 165
110 air. Finally, because no polymer is perfectly selective, the 166
111 sensors can have undesirable cross-sensitivities.

Various researchers have developed chemical sensors that 112
contain an array of different polymers and/or other selec- 113
tively absorbing compounds on a single, microfabricated 114
chip with multiple transducers [6,8–10,21,22]. Some of 115
these “electronic noses” combine such arrays with pattern 116
recognition algorithms to analyze the outputs of the various 117
sensors [18–20,33–35]. Electronic noses can identify com- 118
plex odors, but are especially sensitive to drift and have 119
to be frequently “trained” (i.e. recalibrated). Examples of 120
commercially available electronic nose instruments include 121
a chemiresistor array from Cyrano Sciences Inc. (Pasadena, 122
CA) and a SAW array from Microsensor Systems Inc. 123
(Bowling Green, KY). In addition, the JCAD chemical war- 124
fare agent sensor from BAE Systems (Rockville, MD) is 125
essentially an electronic nose also based on polymer-coated 126
SAW sensors. 127

1.2. Chemicapacitive sensors 128

A “chemicapacitive” sensor (or “chemicapacitor”) is a ca- 129
pacitor that has a selectively absorbing material, such as a 130
polymer, as a dielectric: chemicals absorb into the dielec- 131
tric, alter its permittivity, and thereby raise or lower the ca- 132
pacitance of the sensor. Polymer-based chemicapacitors in 133
particular are a promising platform for low-cost, low-power 134
sensors, since unlike most other VOC sensors they do not re- 135
quire heating, mechanical excitation, or light sources. How- 136
ever, chemicapacitors are not limited to polymer dielectrics. 137
Other materials have been used to broaden the range of de- 138
tectable chemicals—sol–gel chemicapacitors, for example, 139
can detect carbon dioxide [23]—although such materials of- 140
ten have to be heated to achieve optimal performance. 141

To date, chemicapacitors have been developed in two ge- 142
ometries. *Interdigitated electrodes* [22–25,29] consist of sin- 143
gle layer of metal deposited on a substrate to form two 144
meshed combs. Polymer is deposited on top of the combs. In 145
one example [22], the combs have a periodicity of 1.6 μm , 146
overall dimensions of 0.8 mm \times 0.8 mm, and capacitance 147

We have developed a micromachined parallel-plate 159
chemicapacitor (Fig. 1) that, unlike previous parallel-plate 160
chemicapacitors, has a fixed gap width and makes it possi- 161
ble to construct an array of different capacitors on a single 162
chip. These micromachined chemicapacitors are signifi- 163
cantly smaller than previous chemicapacitors, so more of 164
them can be integrated on a single sensor chip. In addition, 165

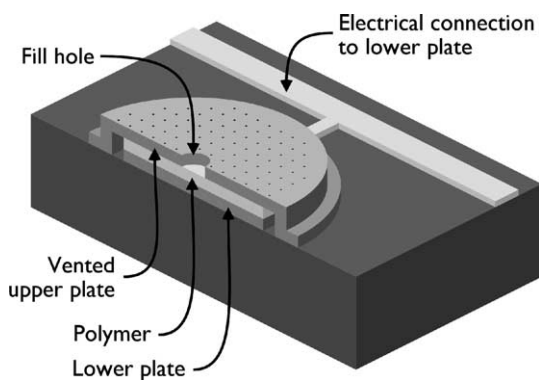


Fig. 1. Diagram of a micromachined parallel-plate chemicapacitive sensor.

166 the response characteristics of our micromachined chemi-
 167 icapacitors are highly reproducible from device to device
 168 since the amount of polymer deposited is not critical; excess
 169 polymer lies outside the gap and does not affect sensor
 170 performance [25,29]. Parallel-plate capacitor sensors should
 171 have twice the sensitivity of interdigitated-electrode sensors,
 172 since in the latter, half of the electric field lines pass en-
 173 tirely through the substrate rather than the polymer. On the
 174 other hand, parallel-plate capacitors are more complex to
 175 manufacture, and they have a longer response time since the
 176 polymer is partially covered with the capacitor plate, reduc-
 177 ing the surface area available for vapor exchange [25,29].

178 In this paper we describe the sensitivity and selectivity
 179 characteristics of these micromachined parallel-plate chemi-
 180 icapacitors. We also discuss how the novel response char-
 181 acteristics of these sensors could be used to enhance the
 182 selectivity of VOC sensor systems.

183 2. Experimental

184 2.1. Sensor elements

185 Sensor chips (Fig. 2) were fabricated in the Multi-User
 186 MEMS Process (MUMPs; JDS Uniphase, Research Triangle
 187 Park, NC). All sensor chips measured 5 mm × 2 mm and had
 188 10 parallel-plate capacitors that could each receive a differ-
 189 ent coating. The capacitor plates were made of conductive
 190 polycrystalline silicon consisting of a 0.5 μm-thick bottom
 191 plate resting on the substrate, an air gap that was filled with
 192 polymer subsequent to the MEMS fabrication process, and a
 193 2 μm-thick ventilated top plate. The capacitor plates were
 194 either circular or square. Circular plate capacitors measured
 195 360 μm in diameter, with a 2 μm gap and a base capaci-
 196 tance of about 0.5 pF. Square plate capacitors measured 300
 197 or 150 μm on a side, with a 0.75 or 2.0 μm gap and base
 198 capacitances of 0.1–1.0 pF.

199 To minimize flexing of the top plate when the polymer
 200 absorbed VOCs and swelled, the top plate was anchored to
 201 the substrate with posts at approximately 60 μm intervals.
 202 The top plate also had 2 μm diameter etch holes separated

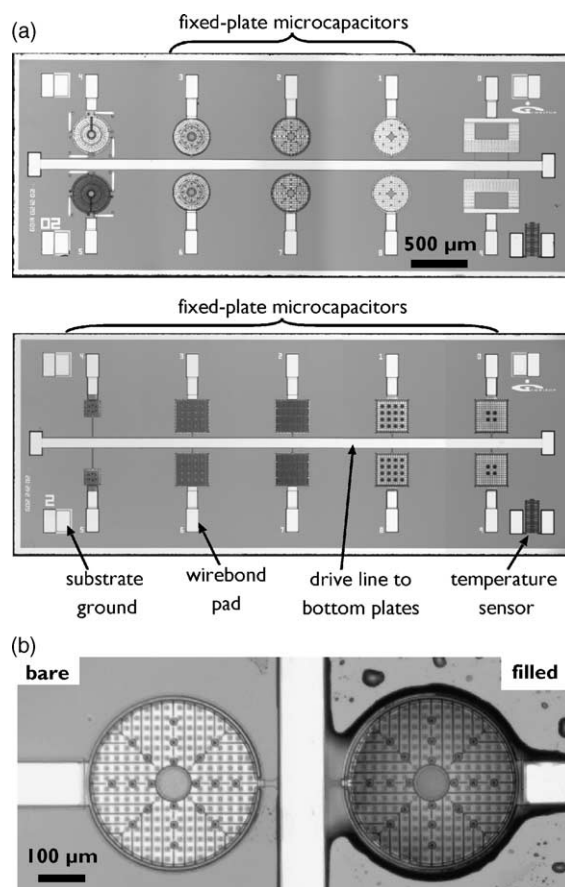


Fig. 2. (a) Two sensor chips showing various sensor designs. (b) Typical sensors on the same chip before and after polymer deposition.

203 by about 30 μm. These holes were required for removal of
 204 a sacrificial silicon oxide layer during fabrication but also
 205 allowed analyte vapors to pass through.

206 The gap between the plates was filled with a polymer
 207 injected either from the edge of the device, through the etch
 208 holes, or through larger fill holes in the top plate. Various
 209 etch and fill hole patterns were tested to optimize ease of
 210 coating. For example, some capacitors had many small fill
 211 holes instead of one large fill hole to ensure complete filling
 212 of the device.

2.2. Readout electronics

213
 214 The readout electronics have been described in a previous
 215 publication about capacitive cantilever-based sensors [16].
 216 The readout electronics were identical for the cantilevers
 217 and the fixed-plate capacitors, since both devices had the
 218 same base capacitance. Also as with the cantilevers [16]
 219 the fixed-plate capacitors are intrinsically explosion-safe; the
 220 electrical power available to and stored in the sensor chip is
 221 insufficient to cause a VOC explosion.

222 In brief, a charge/discharge readout circuit [8,16] (Fig. 3)
 223 measured the capacitance of each sensor array using a
 224 10 kHz charge/discharge drive voltage, and produced a

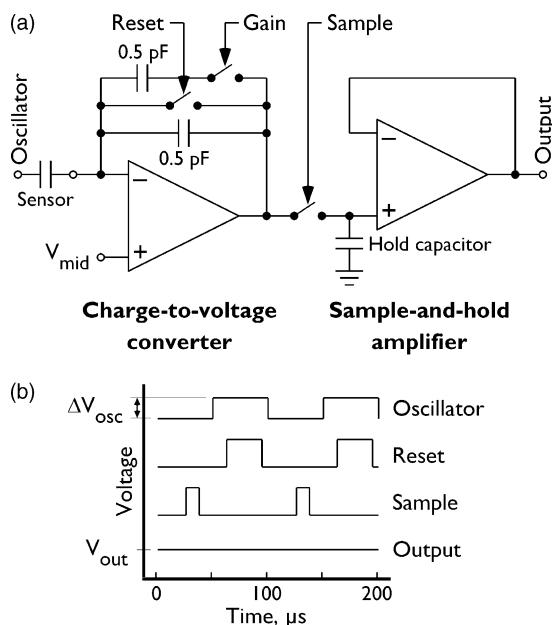


Fig. 3. (a) Diagram of the charge/discharge readout circuit. Opening or closing the “Gain” switch sets the feedback capacitance, C_{feedback} , to 0.5 or 1.0 pF, respectively. (b) Control and output waveforms for the readout circuit.

225 corresponding output voltage, V_{out} :

$$226 \quad V_{\text{out}} = V_{\text{mid}} + \Delta V_{\text{osc}} \frac{C_{\text{sensor}}}{C_{\text{feedback}}} \quad (1)$$

227 where V_{mid} is a virtual ground voltage, ΔV_{osc} the amplitude
 228 of the oscillator drive voltage, C_{sensor} the capacitance of the
 229 capacitive sensor, and C_{feedback} is the feedback capacitance.
 230 The value of the feedback capacitance is either 1 or 0.5 pF,
 231 and is determined by the position of the gain switch. In the
 232 circuit, the feedback capacitor is charged as the sensing cap-
 233 acitor discharges. In general, ΔV_{osc} was set between 0.2
 234 and 1.0 V with V_{mid} being set to 1.8 V, but the settings varied
 235 according to polymer type and the desired sensitivity
 236 and detection range. While increasing ΔV_{osc} could increase
 237 the sensitivity of the capacitors, it could also increase the
 238 noise level if ΔV_{osc} was near 1 V. The timing of the reset
 239 and sample voltage waveforms, required to make the sensor
 240 capacitance measurement, was set by the microcontroller,
 241 and the measured output was an analog voltage.

242 The sensor and readout chips were packaged in a
 243 custom-made dual inline package (DIP) with the readout
 244 chip in a hermetically sealed cavity and the sensor chip in
 245 a second, exposed cavity. The remainder of the readout cir-
 246 cuit [16], or “motherboard” (Fig. 4) contained a socket for
 247 the DIP, a microcontroller and a 12 bit ADC to digitize the
 248 output of the readout chip, and could be made quite small.
 249 For each data point acquired, 256 ADC readings were aver-
 250 aged together to achieve effective 16 bit resolution. The
 251 smallest measurable capacitance change was 0.25 fF.

252 The relative permittivity, or dielectric constant of the se-
 253 lectively absorbing polymer was calculated by comparing

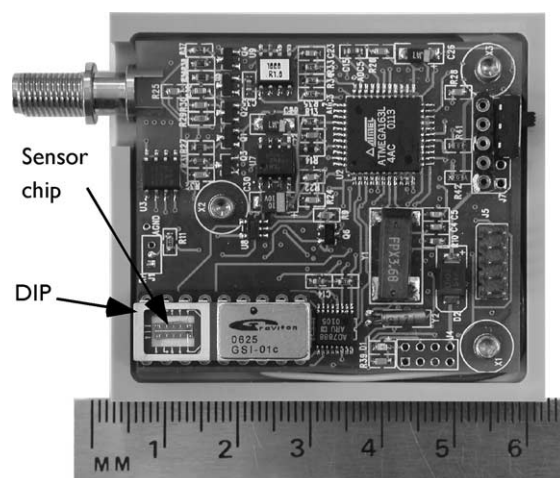


Fig. 4. A sensor unit as tested. The sensor chip in its 18-pin package is visible at the lower left corner of the motherboard. The antenna connector at top left is for wireless I/O capabilities that were not used for the present work.

the output voltage of filled and unfilled capacitors in the absence of VOCs:

$$254 \quad \varepsilon_{\text{polymer}} = \frac{(C_{\text{sensor}})_{\text{filled}}}{(C_{\text{sensor}})_{\text{unfilled}}} \quad (2) \quad 255$$

256 where $(C_{\text{sensor}})_{\text{unfilled}}$ is the capacitance of the capacitor with
 257 air in the capacitor gap, and $(C_{\text{sensor}})_{\text{filled}}$ the capacitance
 258 with polymer in the gap. Assuming that C_{feedback} and ΔV_{osc}
 259 are constants, solving Eq. (1) for C_{sensor} and substituting
 260 into Eq. (2) leads to:

$$261 \quad \varepsilon_{\text{polymer}} = \frac{(V_{\text{out}} - V_{\text{mid}})_{\text{filled}}}{(V_{\text{out}} - V_{\text{mid}})_{\text{unfilled}}} \quad (3) \quad 262$$

263 2.3. Polymers

264 Polymers and synthesis precursors were purchased
 265 from Polysciences Inc. (Warrington, PA), Scientific Poly-
 266 mers Inc. (Ontario, NY), Gelest Inc. (Morrisville, PA), or
 267 Sigma–Aldrich (St. Louis, MO). Polymers were selected
 268 based on their ability to selectively form weak reversible
 269 chemical interactions (hydrogen bonds, van der Waals
 270 bonds, and dipole–dipole interactions) with a particular an-
 271 alyte [1–5,36–40]. In general, liquid polymers or polymers
 272 with a low modulus of elasticity were preferred because
 273 they absorb analytes more quickly than rigid polymers [3].

274 Experiments were carried out with eight liquid and solid
 275 polymers (Table 1), all of which have been used in previous
 276 VOC sensors [3,4,18,19]. Polymers were chosen based on
 277 the findings in the literature applying these solubility pa-
 278 rameters. Other factors in choosing the polymers included
 279 stability, ease of acquisition, solubility in a suitable solvent
 280 and ease of coating application. The fluoroalcohol SXFA
 281 [36] has an affinity for hydrogen-bonding bases and is
 282 useful for the detection of chemical warfare agents such
 283 as Sarin. SXFA was synthesized in house from methods

Table 1
Polymer properties and deposition parameters

| Polymer | Properties | | | Deposition | |
|--|----------------------------------|---|--|-----------------------|----------------------|
| | Polymer phase (at 50% RH, 20 °C) | Analytes | Measured dielectric constant (in dry N ₂ , 20 °C) | Solvent | Concentration (wt.%) |
| Polyisobutylene (PIB; 1350 MW) | Liquid | Nonpolar hydrocarbons | 2.1 ± 0.09 | Toluene | 1.0 |
| Polydimethyl siloxane (PDMS; 100,000 cSt) | Liquid | Nonpolar hydrocarbons | 2.5 ± 0.07 | Chloroform or toluene | 1.0 |
| Polycarbonate urethane (PCUT) | Solid | Low polarity hydrocarbons | 4.0 ± 0.26 | Chloroform | 1.0 |
| Polyethylene-co-vinylacetate with 40% acetate content (PEVA 40%) | Solid | Low polarity hydrocarbons; aromatics | 4.1 ± 0.04 | Toluene or chloroform | 0.75 |
| Siloxanefluoro alcohol (SXFA) | Liquid | Polar VOCs; hydrogen-bonding bases | 7.3 ± 0.08 | Chloroform | 1.0 |
| Polyepichlorohydrine (PECH; 700,000 MW) | Gum | Low polarity hydrocarbons; chloroethers | 7.4 ± 1.1 | Chloroform | 0.2 |
| Cyanopropyl methyl phenylmethyl silicone (OV-225; 9000 cSt) | Liquid | Nitro-aromatics; aromatic VOCs | 11.0 ± 0.5 | Toluene or chloroform | 1.0 |
| Dicyanoallyl silicone (OV-275; 20,000 cSt) | Liquid | Nitro-alkanes; polar VOCs | 33.1 ± 3.7 | Acetone | 1.0 |

found in the literature. Dicyanoallyl silicone (OV-275) and cyanopropyl methyl phenylmethyl silicone (OV-225), are siloxane-based commercial chromatography stationary phases that can be used to detect byproducts and impurities found in explosives [41]. Polyethylene-co-vinylacetate (PEVA), polyepichlorohydrin (PECH), polycarbonate urethane (PCUT), polyisobutylene (PIB), and polydimethyl siloxane (PDMS) are used to detect VOCs with moderate to low polarity values.

Since literature values were not available for many of the polymers used in these experiments, relative permittivity values (Table 1) were measured according to Eq. (3). The literature values of 2.1–2.4 for PIB and 3.0 for PDMS [39] roughly agree with our measurements. However, the measured dielectric constants for high-polarity polymers such as SXFA, OV225, and OV275 may be less accurate because they approach the limit of the detection electronics and these highly polarizable polymers allow charge to leak through the capacitors during the measurement process.

2.4. Polymer deposition

Polymer solutions (Table 1) were deposited onto the sensors with a manually positioned piezoceramic inkjet head (Microfab Technologies MJ-AB01-030 30- or 80-micron dispenser with CT-M3-01 inkjet controller). The inkjet head could deposit individual droplets (30–100 μm diameter) of solution, each of which dried in about 1 s.

Solutions were mixed to a concentration that did not clog the inkjet nozzle (indicating that the solution was too concentrated) or wash away previously deposited polymer (too dilute). The solution concentrations ranged from 0.015 to 2% by weight of polymer in solvent (optimal values are in Table 1). Both the voltage waveform applied to the inkjet (controlling the droplet size) and the amount of time between

droplets, were optimized for each combination of capacitor geometry and polymer type.

Sensor capacitance was monitored during deposition, and each capacitor was coated until its capacitance stopped changing, i.e. until the entire gap was filled. Typically, this entailed depositing 100–300 droplets of a solution containing 1.0 wt.% dissolved polymer. Since the droplets were so small, most of the solvent would evaporate before the next drop landed. The sensors were subsequently dried in an oven at 110 °C for 30–60 min to completely remove the solvent. After drying, the sensors were visually inspected under a microscope and their capacitance levels were measured to determine if additional polymer was needed to fully fill the gap between the plates. The drying process was repeated after each application of polymer. A small amount of material would remain on top of the top capacitor plates.

Coatings were typically applied to seven “signal” capacitors, leaving one uncoated “reference” capacitor and two unused, unconnected capacitors. The uncoated capacitors did not respond to chemical exposures or changes in relative humidity or flow rate. To reduce systematic common-mode electronic noise, the reference output was subtracted from each of the seven signal outputs. Typically this noise level was reduced from near 1 mV to approximately 0.3 mV, when ΔV_{osc} was 0.2–0.7 V.

2.5. Sensor test system

The sensors were tested in custom-made stainless steel environmental chambers. A large chamber with internal dimensions of 10 cm × 15 cm × 6 cm could accommodate two packaged sensor chips with their electronics. A smaller chamber measuring 2.5 cm × 7.6 cm × 0.8 cm, which could accommodate two packaged sensors, with the sensor read-out electronics outside the chamber, was used for achieving faster vapor delivery. The small-volume chambers were

352 treated with the Silcosteel[®] process (Restek Corporation, 402
353 Bellefonte, PA) to prevent chemical contamination. A re- 403
354 circulating chiller that pumped water through cold plates or 404
355 water jackets around the chamber regulated the temperature 405
356 of each chamber. Each chiller had a closed-loop tempera- 406
357 ture control system regulated by a four-wire RTD inside the 407
358 chamber. Humidity inside the chamber was monitored with 408
359 a Honeywell HIH-3602-C humidity sensor (Honeywell Inc., 409
360 Freeport, IL).

361 All VOCs were purchased commercially (Sigma–Aldrich; 410
362 Alfa Aesar, Ward Hill, MA; Fisher Scientific Inc.; or VWR 411
363 International Inc., West Chester, PA) and used as received. 412
364 VOC vapors were generated by bubbling nitrogen or air 413
365 through gas-washing bottles (bubblers) containing liquid 414
366 VOCs. To control the VOC concentration, the glass bub- 415
367blers were immersed in a water bath; the temperature of 416
368 the bath could be adjusted to vary the vapor pressure of 417
369 the VOC. Furthermore, the output of the bubblers was di- 418
370 luted with air or nitrogen metered by mass-flow controllers 419
371 (MKS Instruments, Andover, MA). Humidity was similarly 420
372 controlled by passing a metered percentage of the nitrogen 421
373 or air flowing into the test chamber through a bubbler con- 422
374 taining water. A LabVIEW (National Instruments, Austin, 423
375 TX) program varied the temperature, humidity, and con- 424
376 centration of up to six analytes inside the chamber while 425
377 recording the output from the sensor units. 426

378 2.6. Sensor response time

379 To gauge the differences in response times between liquid 428
380 and solid polymers, a set of tests was performed with the 429
381 coated sensors placed perpendicular to the outlet of a diluted 430
382 vapor stream immediately after a four-way switching valve. 431
383 For this experiment, OV225, SXFA and PEVA were cho- 432
384 sen as representative liquid and solid polymers. Each sen- 433
385 sor chip was tested individually, and placed approximately 434
386 1 mm from the outlet tube whose inner diameter was 1/16 of 435
387 an inch. The vapor concentration was 10% of P_{sat} with the 436
388 bubblers held at 15 °C, and the total flow rate was 500 sccm, 437
389 which resulted in a vapor plug that could arrive at the sensor 438
390 in approximately 0.01 s. The electronic four-way switching 439
391 valve was alternated between dry nitrogen and the diluted an- 440
392 alyte vapor and took less than 2 s to switch fully. The coated 441
393 capacitors did not respond to the switching of the valves, 442
394 when there was no analyte present. Vapor generation was 443
395 started 10 min prior to exposure to allow the bubbler tem- 444
396 perature to stabilize. During the experiments the uncoated 445
397 capacitors did not respond to the chemical exposures. 446

398 3. Results and discussion

399 3.1. Sensitivity and response

400 The chemicapacitor sensitivity to most VOCs is gener- 450
401 ally comparable to that of other polymer-based VOC sen- 451

sors. We have observed that the chemicapacitors typically 402
have sufficient sensitivity to detect common industrial sol- 403
vents below 100 parts per million (ppm), and below 1 ppm 404
for the chemical warfare agents simulants and explosives 405
taggants [42]. Table 2 shows the lowest concentration of 406
various analytes—including industrial solvents, chemical 407
warfare agent simulants, and nitro-organics—that we have 408
detected with polymer-filled capacitors. Many of the val- 409
ues in Table 2 reflect the lowest concentration that our test 410
system can deliver, rather than the lowest concentration the 411
sensor can detect. Theoretical limits of detection (LOD) 412
have been calculated using a signal-to-noise limit of 3:1. 413
One can see from the LOD values, that SXFA is more 414
sensitive to the more polar analytes. Four polymers were 415
compared for the detection of CEE; SXFA and OV275 were 416
significantly more sensitive than either PECH or PEVA. 417
As an example of the data from which Table 2 was gener- 418
ated, Fig. 5 shows the response of an SXFA-filled capacitor 419
to various concentrations of dimethyl-methyl-phosphonate 420
(DMMP, a simulant for sarin) in dry and humid air. Both the 421
DMMP and water vapor cause an increase in the measured 422
capacitance; however the sensitivity of SXFA to DMMP 423
vapor is significantly greater than to water vapor. Expo- 424
sure to 800 ppb of DMMP causes a change in capacitance 425
that is more than twice that of a change in 40% relative 426
humidity. 427

The signal-to-noise ratio generally increases with in- 428
creasing polymer and analyte polarity, an effect that will 429
be discussed further in Section 3.3. In our experience, at a 430
given analyte concentration, the signal-to-noise of a chem- 431
icapacitor is roughly proportional to its capacitance. Thus, 432
signal-to-noise improves as plate area increases or as gap 433
width decreases. Although larger capacitors are undesirable 434
because they occupy more area on the sensor chip and 435
therefore cost more to fabricate, smaller gaps have no such 436
disadvantage. In addition, smaller gaps lead to thinner poly- 437
mer films and therefore faster response. Thus, the ideal gap 438
dimension is the smallest that can be filled with polymer. 439
We have successfully filled capacitors with 0.75 μm gaps, 440
which is the narrowest gap achievable with the MUMPs 441
process. Over a testing period of several weeks, we have 442
not observed differences in the stability of capacitors with 443
a 0.75 or 2 μm gap. 444

Although chemicapacitors may exhibit a linear response, 445
particularly when used to measure humidity [24,26,29] in 446
general their response is nonlinear (Fig. 6). McGill et al. 447
[3] have suggested that the response is nonlinear because as 448
the films absorb an analyte, their ability to interact with the 449
analyte changes, generally reducing their capability to ab- 450
sorb more of the same analyte. The ability to absorb other 451
analytes may also be affected; for example, the presence of 452
humidity reduces the sensitivity of an SXFA film to DMMP 453
(Fig. 5). A possible factor contributing to the nonlinear re- 454
sponse may be that as the polymer swells, the reduced poly- 455
mer density between the plates causes a decrease in permit- 456
tivity. This swelling effect counters the effect of adding a 457

Table 2

Lower explosive limit (LEL) and immediately dangerous to life and health (IDLH) concentration for selected VOCs; with lowest detected vapor concentrations and calculated theoretical limit of detection (LOD) in ppm (v/v), signal-to-noise ratio (measured response in volts/peak-to-peak noise in volts), polymer used to achieve the lowest detected concentrations, and oscillation amplitude

| Analyte | LEL (ppm) | IDLH (ppm) | Lowest detected concentration (ppm) | S:N | LOD (ppm) | Polymer used | ΔV_{osc} (V) |
|---|-----------|------------|-------------------------------------|-----|-----------|--------------|----------------------|
| Industrial solvents | | | | | | | |
| Acetone | 25000 | 2500 | 11 | 17 | 2 | SXFA | 0.4 |
| Acetonitrile | 50000 | 500 | 25 | 10 | 8 | SXFA | 0.4 |
| Benzene | 12000 | 500 | 142 | 5 | 85 | OV225 | 0.2 |
| Bromobenzene | 5000 | N/A | 7 | 50 | 0.4 | SXFA | 0.4 |
| Ethyl acetate | 20000 | 2000 | 37 | 20 | 6 | SXFA | 0.4 |
| Ethyl alcohol | 33000 | 3300 | 63 | 12 | 16 | SXFA | 0.4 |
| Isopropyl alcohol | 20000 | 2000 | 84 | 18 | 14 | SXFA | 0.2 |
| Methyl alcohol | 60000 | 6000 | 21 | 9 | 7 | SXFA | 0.4 |
| Octane | 14000 | 1000 | 49 | 5 | 29 | OV225 | 0.2 |
| Tetrahydrofuran (THF) | 20000 | 2000 | 7 | 15 | 1 | SXFA | 0.4 |
| Toluene | 11000 | 500 | 61 | 3.3 | 55 | OV225 | 0.2 |
| Chemical warfare agent simulants | | | | | | | |
| Chloroethylether (CEE) | N/A | N/A | 1 | 3 | 1 | PECH | 0.5 |
| | | | 0.4 | 3 | 0.4 | PEVA | 1.0 |
| | | | 0.2 | 10 | 0.06 | SXFA | 0.4 |
| | | | 2.2 | 10 | 0.07 | OV275 | 0.075 |
| Diisopropyl methylphosphonate (DIMP) | N/A | N/A | 0.1 | 100 | 0.003 | SXFA | 0.4 |
| Dimethyl methylphosphonate (DMMP) | N/A | N/A | 0.18 | 300 | 0.002 | SXFA | 0.4 |
| Explosives byproducts and impurities | | | | | | | |
| Nitro-benzene | N/A | N/A | 0.02 | 13 | 0.005 | SXFA | 0.2 |
| | | | 0.44 | 10 | 0.1 | OV275 | 0.075 |
| Nitro-propane | N/A | N/A | 5 | 25 | 0.6 | SXFA | 0.4 |
| Nitro-toluene | N/A | N/A | 0.001 | 23 | 0.0001 | SXFA | 0.2 |

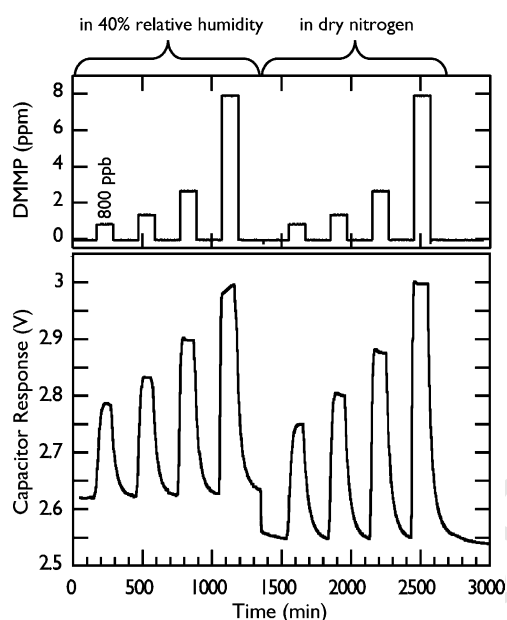


Fig. 5. Response of an SXFA-filled capacitor to low concentrations of DMMP in a background of dry nitrogen and in nitrogen with 40% relative humidity. The sensor was at 30 °C and the oscillation amplitude ΔV_{osc} was 0.1 mV. The response to 800 ppb of DMMP was approximately 167 and 200 mV with and without the background humidity, respectively, and the peak-to-peak noise level was 0.5 mV.

polar analyte and the resulting combination of factors may not be linear with concentration.

The chemicapacitor sensitivity varies with temperature. Increased temperature increases VOC volatility, decreasing the amount that absorbs into the polymer, as shown in Fig. 6. The data are presented as changes in response from baseline at each temperature. The differences in response at the three temperatures are, within error, explained by the differences in vapor pressure. This suggests that, at least within this temperature range, the solubility of acetone into SXFA is not affected by any changes in the polymer. This result is consistent for all of the liquid polymers we have tested in this temperature range.

The responses (Fig. 6) of the SXFA films show that humidity has little influence on the acetone response at low acetone concentrations, however above 15,000 ppm of acetone, the high humidity background causes a larger response from the capacitors. Again, these data are presented as changes from the baseline at each relative humidity. In typical commercial applications, such as industrial leak detection, we expect that an embedded microcontroller will take measurements from a temperature sensor and humidity-sensitive chemicapacitor in addition to the analyte-sensitive chemicapacitor, and then use a multiple-parameter calibration table or pattern recognition algorithm to determine the analyte concentration.

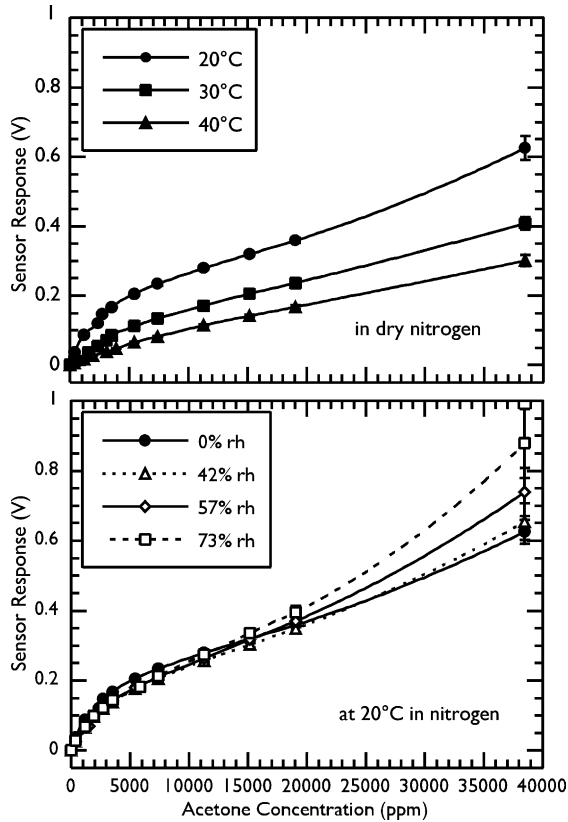


Fig. 6. Average response of four SXFA-filled capacitors to varying concentrations of acetone in dry nitrogen at 20, 30 and 40 °C (upper graph). Average response of the same sensors to varying concentrations of acetone at four different relative humidity levels in nitrogen at 20 °C (lower graph). All four capacitors were on a single sensor chip and were measured with $\Delta V_{\text{osc}} = 0.2$ V. The error bars reflect the standard deviation of the four sensors' responses.

484 3.2. Reproducibility

485 To test the reproducibility of the deposition process, four
 486 identical SXFA-filled capacitors were produced on each of
 487 six sensor chips. These chips were separately given 30 min
 488 exposures of 10% $P_{\text{sat}}(15^\circ\text{C})$ acetone in dry nitrogen at 20
 489 and 40 °C, and their response magnitudes were measured.
 490 The coefficient of variation for the four capacitors on any
 491 single chip averaged 3.2% at 20 °C and 1.9% at 40 °C. The
 492 chip-to-chip variation averaged 9% at 20 °C and 6% at 40 °C.

493 We hypothesize that capacitor-to-capacitor variability de-
 494 creases at the higher temperature because the sensors settle
 495 faster. That is, at higher temperatures, acetone diffuses more
 496 quickly into the polymer, and a capacitor reading is more
 497 likely to be made under a steady-state condition. This re-
 498 duces or removes one source of variability, i.e. differences
 499 in diffusion speed between different capacitors and between
 500 sensor chips.

501 Thus, inkjetting methods can make chemicapacitors that
 502 vary in response by only a few percent. Unlike most other
 503 polymer-based sensors, the structure of the capacitors fixes
 504 the volume being sensed. Changes in the dielectric material

505 due to vapor absorption can take the form of changes in the
 506 volume fraction of polymer and analyte. In addition, as long
 507 as the capacitors are completely filled, their topology will
 508 not affect the capacitor's capacitance. This is an important
 509 advantage of this form of chemicapacitor, potentially elimi-
 510 nating the need to individually calibrate sensors and thereby
 511 reduce production costs.

512 3.3. Response time

513 Many factors influence a polymer coated sensor's re-
 514 sponse time, including mass transport limitations, vapor con-
 515 centration, the stiffness, crystallinity and thickness of the
 516 polymer and the molar volume and diffusivity of the analyte
 517 [43]. In general, large analyte molecules will diffuse
 518 slower through polymers than small molecules. Solid poly-
 519 mers will reduce the rate of analyte diffusion compared to
 520 liquid polymers, and polymers that have a high amount of
 521 crystallinity will also have slower responses compared to
 522 rubbery or amorphous polymers. In fact, it has been shown
 523 that the diffusion constant of molecules can decrease by sev-
 524 eral orders of magnitude for relatively small increases in the
 525 molecules size [43]. Results in the literature suggest that thin
 526 layers of liquid polymers should produce the fastest sensors,
 527 especially with smaller analyte molecules.

528 The response time of our sensors, as shown in Table 3,
 529 generally conforms to this pattern. Both SXFA and OV225
 530 are liquid polymers, while PEVA with 40% vinyl acetate is
 531 a rubber-like polymer with approximately 10% crystallinity
 532 (the crystallinity of PEVA 40% was estimated from data
 533 in [44]). For the three circular plate capacitors that were
 534 tested, the onset of response occurs within 1 s for the four vapors
 535 tested for SXFA and OV225, and within 3 s for PEVA.
 536 Table 3 shows that the time to achieve 10% of full response
 537 (t_{10}) to all four vapors for the two liquid polymers is only
 538 a few seconds to about 20 s, while t_{10} for the solid PEVA
 539 films is typically longer. The time to achieve 90% of full
 540 response (t_{90}) ranges from 20 s for SXFA and acetone, to
 541 many minutes depending on the stiffness of the polymer and
 542 the diffusion of the analyte. In all cases, the liquid polymers'
 543 t_{10} absorption and desorption response was faster than the
 544 solid polymer's responses. In addition, it is apparent that
 545 desorption can be slower than adsorption, especially if the
 546 polymer interacts strongly with the analyte. SXFA in particu-
 547 lar exhibits slower desorption than adsorption, presumably
 548 due to strong acid–base interactions with the analyte.

549 Polymers may “relax” [43] when responding to certain
 550 analytes and especially at large concentrations, i.e. the sig-
 551 nal reaches a maximum and then begins to decline during an
 552 exposure to a constant concentration of analyte. This behav-
 553 ior could occur because the polymer expands and begins to
 554 seep out of the capacitor gap. Relaxation artificially lowers
 555 the 0–90% response time, since the maximum response oc-
 556 curs before the sensor has finished responding to the analyte.
 557 Another factor that could effect the measured response time
 558 for the acetone exposures is evaporative cooling; where the

Table 3

Time to reach 10% (t_{10}) and 90% (t_{90}) of maximum response at 20–25 °C and 0% humidity; average response \pm standard deviation; analyte concentration = 10% of P_{sat} at 15 °C

| Polymer | Analyte | Absorption t_{10} (s) | Desorption t_{10} (s) | Absorption t_{90} (s) | Desorption t_{90} (s) | Response (mV) |
|---------|---------|----------------------------|----------------------------|----------------------------|----------------------------|---------------------|
| PEVA | Toluene | 14.3 | 18.6 | 366 | 510 | -90.8 ± 4.6 |
| | Acetone | 21.1 | 10.0 | 312 | 378 | 40.8 ± 6.6 |
| | DMMP | 65 | 49.2 | 1548 | 1812 | 3.9 ± 0.3 |
| | Water | – | – | – | – | Negligible response |
| SXFA | Toluene | 2.6 | 3.9 | 318 | 690 | 172.8 ± 12.8 |
| | Acetone | 4.2 | 3.2 | 19.8 | 228 | 750.0 ± 23.7^a |
| | DMMP | 15.8 | 11.0 | 138 | 3084 | 1170.8 ± 3.5 |
| | Water | 3.7 | 9.12 | 636 | 2016 | 78.3 ± 10.3 |
| OV225 | Toluene | 8.6 | 13.8 | 168 | 396 | -27.0 ± 1.4 |
| | Acetone | 2.1 | 2.2 | 84 | 84 | 44.8 ± 5.0 |
| | DMMP | 2.9 | 6.7 | 558 | 402 | 66.8 ± 5.7 |
| | Water | – | – | – | – | Negligible response |

^a 4.3% relaxation in 1 h.

559 temperature of the liquid acetone decreases when high flow
560 rates are pushed through the bubbler. Even a small amount
561 of cooling could have lead to a measurable reduction in va-
562 por concentration at the sensors.

563 The diffusion path length also affects response time [45].
564 The distance that analyte molecules need to diffuse in our
565 micromachined capacitors is determined by the thickness of
566 the polymer film and by the number and density of etch
567 holes. Making larger etch holes, or increasing the number
568 of etch holes would greatly increase the open surface area
569 for vapor exchange, and reduce the distance that the analyte
570 would have to diffuse. The density of etch holes in our cur-
571 rent devices is very low, and response time would be greatly
572 improved by reducing the distance between etch holes to the
573 MUMPs design limit of 2 μm . In addition, residual polymer
574 remains on top of the capacitors in our method of deposition,
575 which can also slow the sensor response by acting as an ad-
576 ditional diffusion path for the analyte. We have not yet deter-
577 mined a satisfactory method to remove the residual polymer.

578 3.4. Response mechanism

579 As Eq. (3) illustrates, the output of a chemicapacitor re-
580 flects the permittivity of its selectively absorbing dielectric.
581 The sensor responds to chemicals when the dielectric ab-
582 sorbs an analyte, causing its permittivity to change. Hierle-
583 mann et al. [22] have previously hypothesized that a com-
584 plex combination of response phenomena occurs and that
585 the degree of change depends on four factors: (1) dielectric
586 chemical structure modification from reversible weak inter-
587 actions (hydrogen, dipole, van der Waals) with the analyte;
588 (2) the amount of swelling that the dielectric undergoes upon
589 absorbing the analyte (swelling reduces the density of dipole
590 moments within the polymer, and therefore the permittivity
591 of the polymer); (3) the permittivity of the analyte being ab-
592 sorbed; and (4) the amount of analyte that absorbs into the
593 dielectric.

594 Unlike the interdigitated design of Hierlemann et al. [22],
595 in the present design, the fixed parallel-plate structure that
596 we have employed causes all of the electric field lines to pass
597 through the polymer between the plates. Consequently, the
598 measured capacitance is only dependent on the properties
599 of the material between the plates, which is a fixed volume.
600 Upon vapor absorption the polymer can swell through both
601 the fill holes and vent holes, and the electric field will then
602 pass through a polymer with lower density than in its neat
603 state. Therefore, swelling alone would cause the capacitance
604 to decrease. In contrast, the absorption of any analyte with-
605 out concurrent swelling, whether it has a higher or lower
606 dielectric constant than the polymer will increase the capaci-
607 tance of the device, because it is an additive effect. The ca-
608 pacitance of the device upon vapor exposure can thus either
609 increase or decrease, depending upon whether the swelling
610 or chemical absorption dominates.

611 Two capacitors on the same chip with different gaps were
612 coated with PIB and tested against octane and toluene va-
613 pors. The results, shown in Fig. 7, show a larger response
614 from the 0.75 μm gap device versus the 2.0 μm gap device.
615 The noise level during the experiment was ± 0.15 mV for
616 both devices. This suggests that the sensing gap can be ma-
617 nipulated if needed to achieve greater signal-to-noise levels.
618 The response of PIB to stepped concentrations of octane and
619 toluene shows a change in direction associated with the per-
620 mittivity of the each analyte compared to the polymer. For
621 octane swelling dominates the sensor response, and the over-
622 all capacitance decreases, while with toluene, which has a
623 slightly higher permittivity than octane, the capacitance in-
624 creases. This effect has been observed in several polymers
625 with a variety of permittivity values, resulting in a relative
626 sensitivity pattern that shifts direction depending upon the
627 polarity of the polymer and analyte and on the polymer's
628 ability to swell. In this example, PIB has a solubility pa-
629 rameter [39] ($\delta = 15\text{--}16.5 \text{ MPa}^{1/2}$) and a dielectric constant
630 ($\epsilon = 2.1\text{--}2.4$) that are between the values for octane ($\delta =$

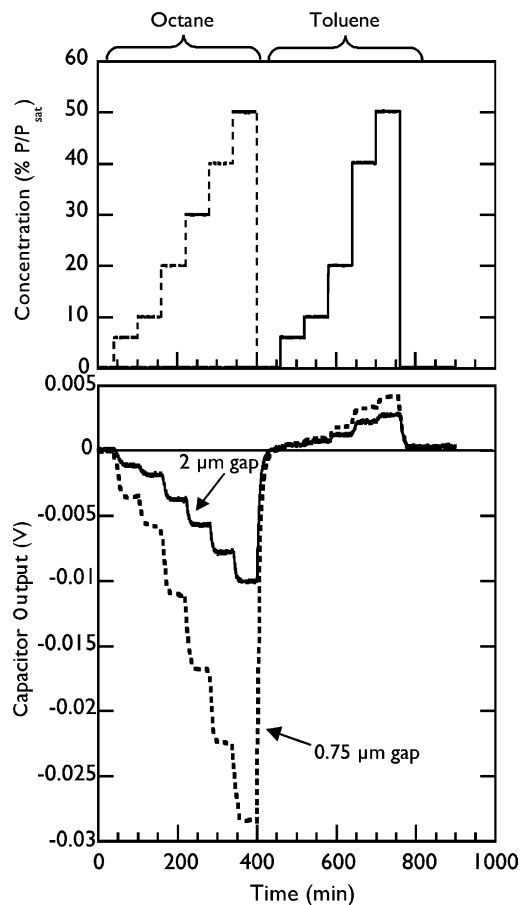


Fig. 7. Response of two PIB-filled chemicapacitors on the same sensor chip to octane and toluene vapors in dry nitrogen at 20 °C (lower graph). The capacitor that produced larger responses (both positive and negative voltage shifts from baseline) has a 0.75 μm gap, while the other has a 2 μm gap. Concentrations are given as a percent of the saturated vapor pressure of the VOCs at 15 °C (upper graph). Both capacitors were measured with the same electronic settings.

631 14.1–15.5 MPa^{1/2}, $\epsilon = 1.95$) and toluene ($\delta = 18.3$ MPa^{1/2},
 632 $\epsilon = 2.4$). From these solubility parameter values, both octane
 633 and toluene would be expected to cause a large amount
 634 of swelling in the PIB coating [1,4,5].

635 To further illustrate the response characteristics of
 636 polymer-filled chemicapacitors, sensor response is plotted
 637 as a function of polymer permittivity and analyte permittivity
 638 in Fig. 8. It is apparent that, in general, high-permittivity
 639 analytes produce larger responses than low-permittivity
 640 analytes, and low-permittivity analytes such as octane can
 641 produce negative responses. The negative sensor responses
 642 (decreases in relative permittivity) arise when the permittivity
 643 of the absorbed analyte is insufficient to compensate for the
 644 swelling that the polymer undergoes upon absorbing the
 645 analyte. In general, low-permittivity analytes are difficult
 646 to sense because they only produce small responses when
 647 they are absorbed.

648 For example, previously reported swelling and mass-uptake
 649 experiments [3,4,38,40,46] indicate that the polymers PIB

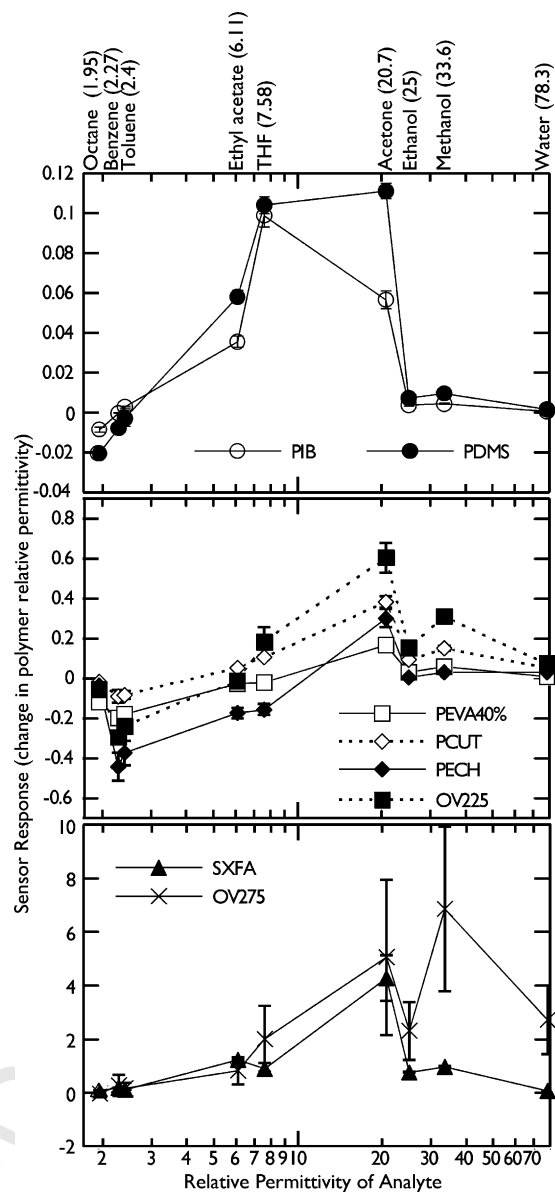


Fig. 8. Sensor response as a function of polymer and analyte permittivity. Each data point was generated from between three and six identically prepared sensors, each of which was exposed to three–five doses of analyte. The data points represent averaged values and the error bars reflect the standard deviation of these values. The concentration of all analytes was 20% of the saturation vapor pressure at 15 °C. All measurements were taken at 0% humidity and 20 °C.

and PDMS should absorb octane, benzene, and toluene
 more readily than they absorb THF. However, in PIB and
 PDMS-filled chemicapacitors, octane, benzene and toluene
 actually produce much smaller responses than THF. This is
 presumably because the dielectric constant of THF is about
 three times higher than that of octane, benzene, or toluene.

Fig. 9 shows the data from Fig. 8 for the PIB-filled capacitor
 with comparable data from the literature for a PIB coated
 chemiresistor [47]. Both data sets have been normalized to
 show them on the same scale. The differences in the data

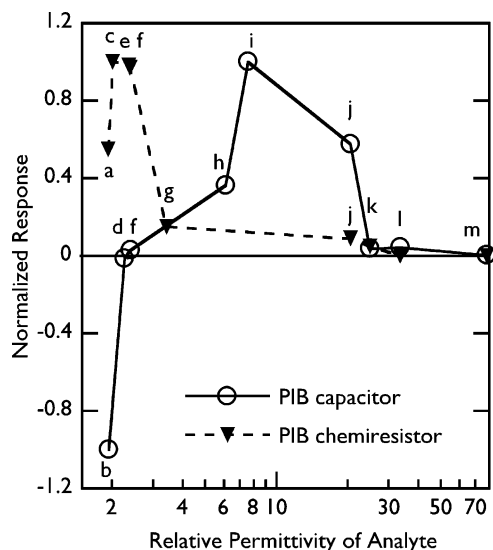


Fig. 9. Response data from Fig. 8 for a PIB-filled chemicapacitor and a PIB/carbon composite chemiresistor from [47]. The chemiresistor data are responses to exposures of each analyte at 10% of P_{sat} at 23 °C. Both data sets are normalized for comparison. Responses to the same and similar VOCs are plotted vs. the dielectric constants of the VOCs at 25 °C (identified by letters on the graph): (a) *iso*-octane (1.94); (b) *n*-octane (1.95); (c) cyclohexane (2.02); (d) benzene (2.27); (e) xylene (2.37); (f) toluene (2.4); (g) trichloroethylene (3.42); (h) ethyl acetate (6.11); (i) tetrahydrofuran (7.58); (j) acetone (20.7); (k) ethanol (25); (l) methanol (33.62); (m) water (78.3).

for the two devices, implies that response depends on different mechanisms. It is generally accepted that the response of polymer-composite chemiresistors is primarily caused by swelling [4,5] which produces the largest responses for analytes whose solubility parameters most closely match the polymers. The chemicapacitor exhibits a large decrease in capacitance when exposed to octane, a very small decrease to benzene, and an increase in capacitance due to toluene and higher dielectric constant analytes (shown in Fig. 8). From relatively large response of the chemiresistor to xylene and toluene, one would expect PIB to swell greatly. If swelling was the primary contributor to the chemicapacitor's response, one would expect a similar response profile (i.e. a large response to toluene). However, the chemicapacitor shows only relatively small responses for analytes within this range of dielectric constants. We speculate that resulting capacitance shift is due to a combination of swelling and the added permittivity due to the absorbed analyte.

In fact, the response characteristics of the low-permittivity polymers PIB and PDMS are dominated by polarity effects. Analytes with relative permittivity values under 3 produce small or negative signals because their permittivity is low and the absorbed amount is insufficient to counteract the large amount of swelling. On the other hand, we observe that analytes with dielectric constants between 3 and 21 produce large signals, even though they may not absorb as well, because their permittivity is high. Finally, analytes with dielectric constants above 22 produce small signals because

PIB and PDMS are low-polarity polymers and do not absorb such high-polarity analytes well, i.e. their solubility parameters do not match [1,4,5].

In contrast, the high-polarity polymer OV275 absorbs high-polarity analytes well, producing large signals in response to methanol and water. Although SXFA also has a high polarity, its acidic hydrogen-bonding character [3] results in low absorption of water and methanol. Neither OV275 nor SXFA absorbs enough octane vapor to produce a negative response from swelling. PEVA, PCUT, PECH, and OV225 exhibit larger negative responses to benzene than to octane, presumably due to greater swelling in the presence of benzene.

While this study is by no means a comprehensive study of the wide variety of polymers available for testing, the results show that a simple array of such coatings could satisfy the needs for a wide range of VOC detection applications.

4. Conclusion

We have shown that micromachined, parallel-plate capacitors can be filled with polymers and used to detect VOCs, chemical warfare agent simulants, and explosive taggants. Chemicapacitors are uniquely selective among polymer-based VOC sensors in that they offer selectivity due to the characteristic electrical properties of the analyte in addition to the selective sorption due to the polymer/analyte interactions. This unique sensitivity of chemicapacitors to analyte permittivity can potentially lead to sensor systems with improved selectivity. In particular, varying response characteristics can be ensured by contrasting the different detection modalities of a polymer-filled chemicapacitor with that of a mass-sensitive transducer, such as a microcantilever, coated with the same polymer [22]. Because both transducers can be fabricated on the same chip and coated in a single process, such a combination would be cost-effective and compact.

Acknowledgements

The authors would like to thank R.J. Warmack, C. Britton, D. McCorkle, and M. Dotson for their technical assistance and discussions and William Ahn for his assistance with mechanical design. The majority of this work was funded internally by Graviton, and also by SBIR contract #N41756-02-M-2038 topic #N01-145.

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884 Biographies

885 *Sanjay Patel* received a BS in chemical engineering from University of
886 California at Berkeley, in 1992. He received his MSE and PhD in chem-
887 ical engineering from the University of Michigan, in 1993 and 1997, re-
888 spectively. His PhD research was on the interactions of combustible gases
889 with metallic and semiconducting thin films on microfabricated hotplates,
890 for use as automotive exhaust gas sensors. In 1997, Dr. Patel became a
891 postdoctoral appointee at Sandia National Laboratories, where he devel-
892 oped chemiresistive polymer-composite films and sensors for the detection
893 of volatile organic compounds; sensor platforms for low-power chemical
894 detection of solvents; and novel diffusion barriers for hydrogen sensors.
895 He joined Graviton Inc., in July 2000 to develop microcantilever-based
896 gas sensors, and helped to develop the chemicapacitive gas sensor tech-
897 nology. In February 2003, Dr. Patel co-founded Seacoast Science Inc.,
898 a sensor development company, located in Carlsbad, CA. Dr. Patel has
899 authored or coauthored several journal articles in the fields of chemical
900 sensing and MEMS.

901 *Todd Mlsna* graduated from Albion College in Albion, Michigan, in 1985
902 with a degree in chemistry. He received his PhD from the University
903 of Texas at Austin in 1990, where he studied organofluorine chemistry,
904 and subsequently became a visiting assistant professor at Clemson Uni-
905 versity. From 1994 until 1998 he worked at the Naval Research Labora-
906 tory (NRL), developing polymer-film-based chemical sensors. His paper
907 “Aromatic Fluoroalcohol Coatings for Explosive Detection” won the Best
908 Paper award at the International Sensor Conference in Beijing in 1998,
909 and the NRL recognized his work on pulsed laser deposition of polymer
910 films in 2000 as one of the year’s best patent applications. Following his
911 time at NRL, he became director of analytical chemistry at Sensor Re-
912 search and Development Corporation, where he developed polymer-based
913 surface acoustic wave sensors. He joined Graviton as a senior staff sci-
914 entist in August 2000, where he developed polymer formulations for mi-
915 crocapacitor sensors. In February 2003, Dr. Mlsna co-founded Seacoast
916 Science Inc., in Carlsbad, CA. Dr. Mlsna has over 60 presentations and
917 publications.

918 *Bernd Fruhberger* has worked in the areas of surface chemical reactions,
919 thin film deposition and spectroscopic characterization of surfaces for over
920 10 years. He received a diploma in chemistry from the University of Hei-
921 delberg in 1989, for studies of oscillating surface reactions, and a PhD in
chemistry, also from the University of Heidelberg, for research on the in-

terface chemistry of metal oxide gas sensors. As a postdoctoral fellow at
Exxon’s Corporate Research Laboratory, he modified transition metal sur-
faces to tailor their reactivities in hydrocarbon surface reactions. He then
held positions as a senior scientist at the BOC Group Technical Center,
where he modified metal surfaces for use in corrosive environments, and
as a senior staff scientist at Sensor Research and Development Corpora-
tion, where he developed thin film metal oxide sensors. Dr. Fruhberger’s
scientific work has led to over 25 publications in peer-reviewed journals,
and numerous presentations at national and international conferences. He
joined Graviton in June 2000 where he developed palladium films for
microcantilever hydrogen sensors. In 2003 he joined the University of
California at San Diego, as a staff researcher where he develops micro-
fabricated sensors and chemically sensitive coatings.

Erno Klaassen’s expertise is in the areas of MEMS and analog inte-
grated circuit design. He received a BS in electrical engineering from the
University of California at Berkeley in 1992, and MS and PhD degrees
in electrical engineering from Stanford University in 1993 and 1996,
respectively. His PhD dissertation, *Micromachined Instrumentation Sys-*
tems, describes a set of fully integrated microsystems built using a novel
micromachining process based on a commercial CMOS process. Presenta-
tions on this work received Best Paper awards at the IEEE Solid State
Circuits Conference and at the International Semiconductor Device Re-
search Symposium. Dr. Klaassen has held positions as analog IC designer
at Analog Devices; as research staff member at the IBM Almaden Re-
search Center, where he developed MEMS and electronics for magnetic
data storage applications; and as senior MEMS and analog designer at
Optical Micromachines, where he was lead designer for a family of bulk-
micromachined MEMS actuators for optical switching applications. Dr.
Klaassen joined Graviton in August 2001 and is currently a senior engineer
at Intel.

Sabina Cemalovic was born and raised in Sarajevo, Bosnia. She graduated
from the Third Gymnasia Chemistry Technical School in 1989 and the
University of Technical Science at Sarajevo in 1993. During these years
she was also a volunteer for the Red Cross in Sarajevo. After spending
1995 in Zagreb, Croatia, in transit to the USA, in 1996 she joined the
American Technology Group in Monrovia, CA. In 1999 she joined Cyrano
Sciences Inc., in Pasadena, CA, where she helped to develop a hand-held
electronic nose. She worked at Graviton from 2000 to 2003 and was
responsible for fabricating and characterizing Graviton’s microcapacitor
sensors. In May 2003, she joined Seacoast Science Inc., as a researcher
to develop chemical sensors.

David Baselt received an MS in chemistry in 1988 from the University of
California at Berkeley, and a PhD in physical chemistry in 1993 from the
California Institute of Technology. As a graduate student, he designed and
constructed one of the first multimode atomic force microscopes, which
was subsequently commercialized by Topometrix Inc. (now ThermoMi-
croscopes). Following a postdoctoral fellowship in video microscopy at
Yale University, he worked at the Naval Research Laboratory developing
microcantilever- and magnetoresistor-based biosensors that use magnetic
forces to measure the strength of intermolecular bonds. This work resulted
in several patents that were later licensed by Graviton; presentations in-
cluding a talk at the 1998 Gordon Conference on Bioanalytical Sensors
and a keynote talk at Biosensors’98; and awards including Best Paper
at Biosensors’98, the Berman award for best applied research paper in
NRL’s chemistry division, and the NRL Technology Transfer award. Dr.
Baselt lead Graviton’s sensor development effort from 1999 to 2003, and
is currently at Stanford Research Systems Inc.