Doped poly (2,5-dimethyl aniline) for the detection of ethanol

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ABSTRACT: Poly (2,5-dimethyl aniline) (P25DMA), with and without NiO and ZnO as dopants, is evaluated as a sensing material for ethanol to detect transdermal ethanol emissions. Three sensing materials—P25DMA, P25DMA doped with 20 wt % NiO, and P25DMA doped with 20 wt % ZnO—are eventually deposited onto a radio frequency identification sensor. The limit of detection for the materials is found to be 3, 24, and 420 ppm, respectively. Also, all three sensing materials are selective toward ethanol with benzene and methanol used as interferents. The response and recovery times are also measured for the three sensing materials and are in the order of seconds, which is acceptable for a transdermal ethanol sensor. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42259.

INTRODUCTION

Driving under the influence of alcohol (ethanol) causes many injuries and fatalities every year.[1] Current methods of ethanol detection use breathalyzers, which are calibrated for an average lung capacity of 2100 cm[3].[2] There are, however, other ways to determine blood alcohol content, such as measuring ethanol emitted from the skin (transdermally). The concentration of ethanol emitted from the skin is much lower than that emitted from breath. Therefore, ethanol sensors for transdermal ethanol must be much more sensitive.[3,4]

With a transdermal ethanol sensor as an eventual target, the sensor must be highly sensitive and selective toward ethanol as well as chemically and thermally stable. The key to a sensitive and selective sensor is the sensing material. Poly (2,5-dimethyl aniline) (P25DMA) was chosen as a sensing material for ethanol since it has high thermal and chemical stability, and affinity toward ethanol.[5] The addition of dopants may improve the sensitivity, selectivity, and response time of a sensing material.[6] Therefore, nickel oxide (NiO)[7] and zinc oxide (ZnO)[8] were chosen as dopants for their catalytic activity toward ethanol. To our knowledge, this is the first time P25DMA has been doped with either NiO or ZnO and used as a sensing material for gaseous analytes.

In this article, five sensing materials were initially evaluated as potential sensing materials for the detection of ethanol. Eventually, the three most promising sensing materials were deposited onto a radio frequency identification (RFID) sensor for further assessment. The lowest level of ethanol detected was 2.5 ppm, low enough for transdermal ethanol detection. The sensing materials were also exposed to two typical interferents (benzene and methanol) to determine their selectivity toward ethanol, since both methanol and benzene are commonly present inside the cabin of a vehicle.[9] Response and recovery times were also measured, as additional characteristics of the sensor response besides sensitivity and selectivity.

MATERIALS AND METHODS

Preparation of Sensing Materials

Poly (2,5-dimethyl aniline) (P25DMA) was synthesized by mixing 2,5-dimethyl aniline, ammonium persulphate, and, if present, the dopants, in deionized water. 2,5-dimethyl aniline (0.39 mL) (A.C.S. reagent, Sigma-Aldrich, Oakville, Ontario, Canada) was added to 20 mL of deionized water and then mixed using a sonicator for 30 min. This solution was then cooled to -1°C before the addition of a solution containing 1.0 g of ammonium persulphate (A.C.S. Reagent, Sigma-Aldrich) in 5 mL of deionized water. The solution was shaken for 1 min to ensure thorough mixing. The mixture was subsequently left to react at -1°C for 6 h.[10] The polymer was filtered out using a funnel and Wattman #5 filter paper and left overnight. The polymer was then washed with ethanol until the liquid ran clear. Finally, the polymer was scraped into a glass vial for storage under atmospheric conditions.
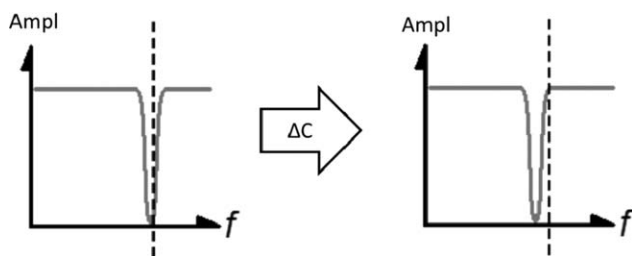
Figure 1. Response schematic of RFID sensor. A change in capacitance (ΔC) results in a change in response amplitude as the resonant frequency shifts.

To obtain the doped polymer, the monomer was polymerized with the dopant suspended in the starting solution. The dopant was added up to 20% by weight with respect to the monomer, before the solution was initially cooled prior to the addition of the ammonium persulphate. Other than the addition of the dopant, which was nickel oxide (NiO) (particle size <50 nm, concentration of 99.8%, from Sigma-Aldrich) or zinc oxide (ZnO) (particle size <100 nm, 50 wt % in water, from Sigma-Aldrich), the polymerization procedure was the same as described above for P25DMA without any dopant.

The P25DMA polymer samples were prepared with two different dopants—NiO and ZnO—at three different concentrations (0% or no dopant, 10 wt % and 20 wt %). In total, five different polymeric sensing materials were prepared for initial screening.

The sensing materials were evaluated using gas analytes in tanks from Praxair (California, USA). These gas analytes (ethanol, methanol, and benzene) were of standard grade, up to 5000 ppm analyte in nitrogen. Nitrogen (5.0 grade, Praxair, Mississauga, Ontario, Canada) was used to dilute the gas analytes to the desired concentrations using the gas test system described in the section titled "Gas Test System".

RFID Sensor

The RFID sensor was composed of an interdigital chemicapacitor and operated at RF. The sensing material was dissolved in N-methyl pyrrolidone and deposited on top of the interdigitated capacitor using a micropipette. Each polymeric sensing material coating was optically inspected using a microscope and measured to be 5 ± 0.5 μm. The polymeric sensing material on

the RFID sensor interacted with the gaseous analytes resulting in a change in the dielectric constant. A change in the dielectric constant caused a shift in the RF resonant frequency, due to a resulting change in capacitance. This was subsequently observed as a change in the response amplitude (Ampl) at a specific resonant frequency (f) (Figure 1). Each sensing material resonates at its own unique resonant frequency.[11]

Gas Test System

A gas test system was designed and constructed that allowed evaluation of both sensing materials and complete sensors at room temperature of 22°C, as described schematically in Figure 2. Gas analytes were mixed, if necessary, using an inline passive mixer, after which the gas line was split using an MKS RS-485 mass flow controller on one side and an MKS 640A pressure controller and MKS 1179A flow meter on the other to ensure a 50 : 50 volumetric split. Both the sensing materials and sensors were tested using a flow rate of 200 sccm. All baselines were measured at 0 ppm (with pure nitrogen) at 200 sccm. Thus, all responses observed were due to physical interactions (absorption and adsorption) between the sensing material and gas analyte and not due to a change in flow rate or gas pressure. Half of the gas stream (200 sccm) was directed into a test chamber that contained the full sensor (sensor with the sensing material). The other half (200 sccm) passed through a flask (with or without a sensing material) and subsequently into a specialized Varian 450 gas chromatograph (GC) with a photon discharge helium ionization detector (PDHID), capable of measuring down to the ppb level for different compounds. The flask could be removed from the system so that the gas stream ran directly into the GC. This allowed for simultaneous parallel measurement of the concentration of gas analyte(s) while a sensor was being tested,[12] for reference purposes.

To test sensing materials, all the gases tested were sent through the flask and into the GC. None went into the sensor test chamber. The gases passed through an empty 250 mL flask en route to the GC to determine the initial concentration of gas. A flask that contained 0.120 g of the sensing material, purged with dry nitrogen for 30 min, subsequently replaced the empty flask. The flask with the sensing material was left on-line for 30 min, which was more than enough time for steady state to be reached. The amount of analyte that interacted with (was sorbed by) the sensing material was ascertained by subtracting
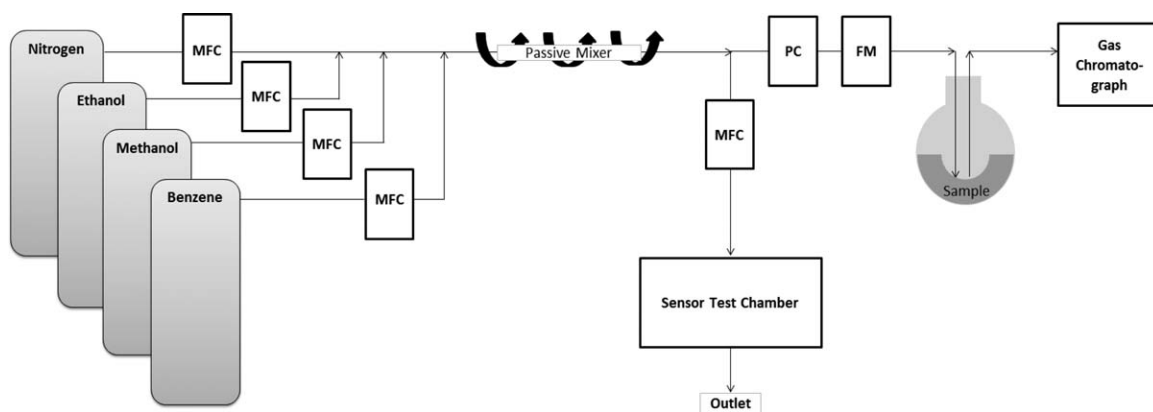
Figure 2. Sensing material test system, where MFC, PC, and FM are mass flow controller, pressure controller, and flow meter, respectively.
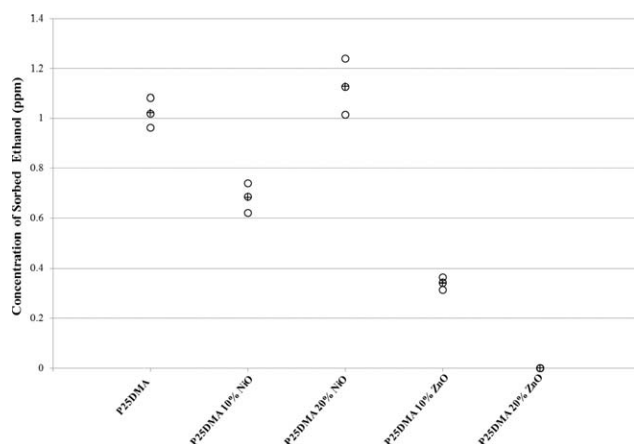
Figure 3. Sorption for each sensing material when exposed to 5 ppm to ethanol.

the concentration of the analyte passing through the flask containing the sensing material (amount not sorbed by the sensing material) from the concentration of the analyte passing through the empty flask (initial concentration). The GC was used as a reliable reference to determine the concentration of analyte(s) that sorbed onto the sensing material.[7]

RESULTS AND DISCUSSION

Ethanol Sorption

To reduce the costly and time-consuming deposition stage onto sensors, five sensing materials were first evaluated based on the

amount of ethanol sorbed. Each sensing material was exposed to 5 ppm of ethanol and the amount sorbed was measured using a GC, as described earlier. Three independent replicates and the corresponding means for each sensing material are shown in Figure 3. Open circles correspond to the measurements, while a plus sign (+) represents the mean.

Based on the results shown in Figure 3, three sensing materials were chosen to deposit onto the RFID sensor: poly (2,5-dimethyl aniline) (P25DMA), poly (2,5-dimethyl aniline) doped with 20 wt % nickel oxide (P25DMA 20% NiO), and poly (2,5-dimethyl aniline) doped with 20 wt % zinc oxide (P25DMA 20% ZnO). Both P25DMA and P25DMA 20% NiO sorbed the most amount of ethanol. P25DMA 20% ZnO was chosen because it had no response to ethanol and, therefore, it could be useful in a sensor array to help determine false positives.

Scanning electron microscopy (SEM) was performed on the sensing materials in order to see potential differences in their structure. Representative SEM micrographs are shown in Figure 4. Figure 4(a) is a micrograph for P25DMA. The layered structure of P25DMA provides a large surface area, and therefore a large number of sensing sites, for the analytes to interact with. Figure 4(b) is a micrograph for P25DMA 20% NiO. The NiO nanoparticles can be seen as the small white dots on the polymer surface in the "zoomed-in" portions, especially the top of Figure 4(b). From these "zoomed-in" areas in Figure 4(b), it can be seen that the NiO nanoparticles are dispersed relatively homogeneously across the polymer. The surface is much rougher for P25DMA 20% NiO than that of P25DMA; however,
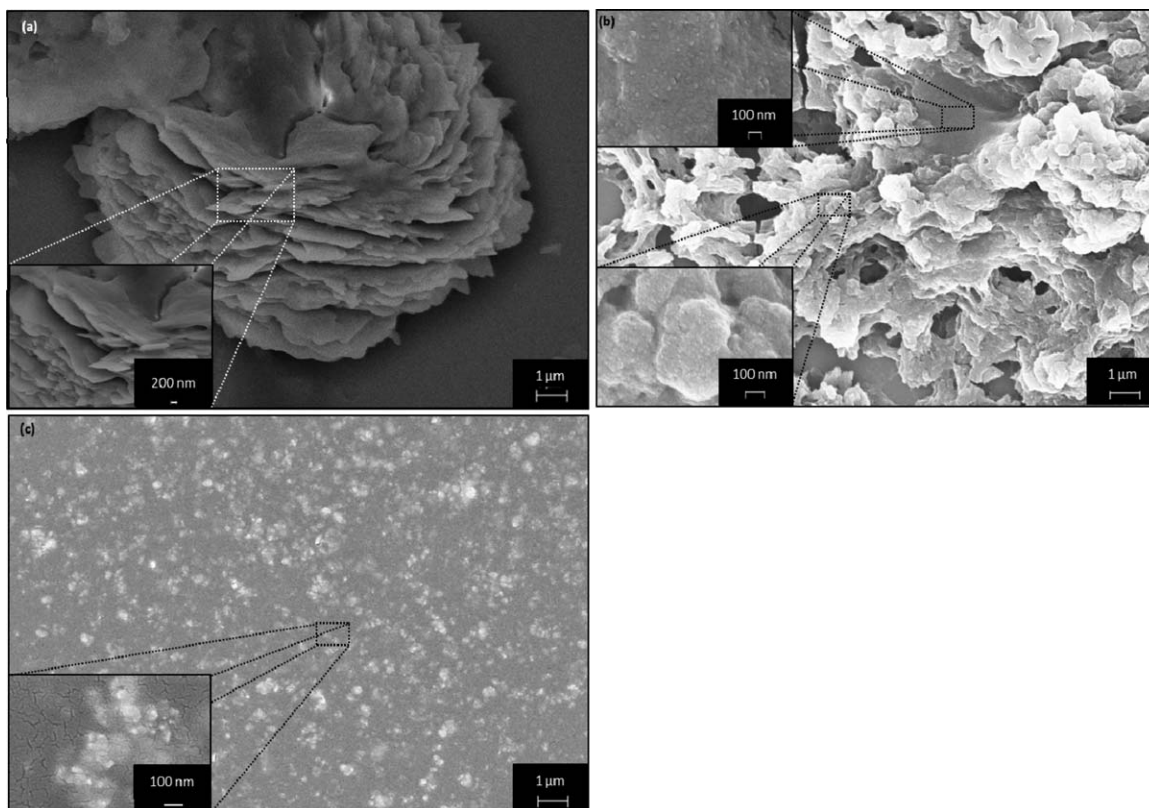
Figure 4. SEM images of (a) P25DMA, (b) P25DMA 20% NiO, and (c) P25DMA 20% ZnO.
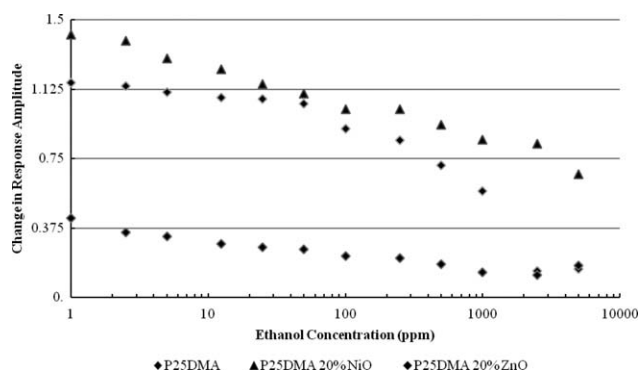
Figure 5. Change in sensor response amplitude (unitless) for each sensing material at different concentrations of ethanol. Note that for clarity, the concentration has been placed on a log scale with a concentration of 0 ppm of ethanol equal to 1 on the scale.

there still is a lot of surface area available for the analytes to interact with. Finally, Figure 4(c) is a micrograph for P25DMA 20% ZnO. It can be seen from Figure 4(c) that the ZnO nanoparticles (white dots) are somewhat homogeneously dispersed, although the ZnO nanoparticles did aggregate, as can be seen in the "zoomed-in" portion of Figure 4(c). This aggregation did not occur for NiO (compare Figure 4(b) for NiO and Figure 4(c) for ZnO). The addition of ZnO nanoparticles to P25DMA certainly resulted in less surface area available to the analytes.

A more porous and/or layered structure, such as that seen for P25DMA and P25DMA 20% NiO, has more sensing sites available to the analyte. Aggregation of nanoparticles also reduces the number of sensing sites available to the analytes due to less surface area of the aggregated nanoparticles exposed to the analytes.

The addition of dopants can change the conformation of the polymer chains, creating "kinks" along the chain.[13] These kinks along the polymer chain could reduce the sensitivity of the sensing material by breaking down the bulk structure, resulting in less surface area or sensing sites available to the analyte. On the other hand, the dopants might also improve sensitivity and selectivity of the sensing material. For example, metal dopants may complex or coordinate with the analyte, thereby providing more sensing sites available to the analyte.[6] The key is finding a balance between these two competing factors. Differences in the structures of the sensing materials were confirmed by SEM, as shown in Figure 4.

The addition of NiO initially reduced the sensitivity (or sorption of the analyte, ethanol) of P25DMA, as one could see from Figure 3, but more NiO (going from 10 to 20 wt % NiO in Figure 3) improved sensitivity (see Sec. 3.2 for more on sensitivity). This was due to NiO's affinity to ethanol that overcame the slight destruction of the P25DMA structure [compare micrographs of Figure 4(a,b)], and hence, overall, increased the sensitivity of P25DMA 20% NiO to ethanol, as shown in Figure 3. The addition of ZnO, on the other hand, significantly reduced the amount of surface area, and thus caused a reduction in sensing sites available to the analyte (ethanol).[14] This reduction in surface area reduced the sensitivity or response to ethanol, which agrees with the results in Figure 3.

Ethanol Sensitivity

Sensitivity is defined as the ability of a sensor to produce a signal when low concentrations of a target analyte are present. The larger the signal, the more sensitive a sensor is. Sensitivity is related to the limit of detection (LoD) of a sensor or sensing material. The LoD of a sensor is considered the lowest detectable concentration of an analyte and is generally taken as three times the noise response.

The three sensing materials chosen from the sorption tests were deposited onto RFID sensors and exposed to ethanol at 12 different concentrations of ethanol (Figure 5). The 12 ethanol concentrations ranged from 2.5 to 5000 ppm of ethanol (in dry nitrogen). It should be noted that ethanol fully saturated P25DMA around 2500 ppm and P25DMA 20% ZnO around 1000 ppm, which can be seen in Figure 5. When saturation occurred, increasing the concentration of analyte exposed to the sensing material no longer produced a change in response.

In these tests, ethanol was the single analyte to be detected. Responses could be observed as low as 2.5 ppm; however, the LoD is calculated relative to the level of noise for each sensing material on the RFID sensor.

The LoD was calculated from (baseline) noise measurements. The sensors were purged with nitrogen for 60 min while recording a measurement every 5 min. Noise was considered to be the standard deviation of the response signal to pure nitrogen. Ultimately, the LoD was calculated as three times the noise (by convention). Results from these calculations are cited in Table I, where the noise response from the sensor was first converted into a concentration of ethanol based on a calibration curve produced from Figure 5, and then multiplied by 3 to get LoD.

Both P25DMA and P25DMA 20% NiO had similar responses to 2.5 ppm of ethanol (as seen from Figure 5); however, the noise for P25DMA 20% NiO was larger. The noise variation observed between sensing materials may have been due to interactions between the analytes and the sensing material or slight changes in the capacitive response of the sensing materials measured by the sensor. A high LoD was expected for P25DMA 20% ZnO based on the results from the sorption tests (seen in Figure 3).

Based on the LoD results shown in Table I, P25DMA has the sensitivity needed for a transdermal ethanol sensor. By optimizing the sensing film thickness, it may be possible to reduce the noise observed for P25DMA 20% NiO and therefore reduce its LoD. Sensitivity of sensing materials and sensors, discussed so far, is a very important characteristic of performance. Aside from sensitivity, an equally important characteristic is selectivity.

Table I. Noise and Limit of Detection for Ethanol for Each Sensing Material on the RFID Sensor

Sensing material	Noise (response)	Noise (ppm)	LoD (ppm)
P25DMA	0.0088	1	3
P25DMA 20% NiO	0.049	8	24
P25DMA 20% ZnO	0.069	140	420
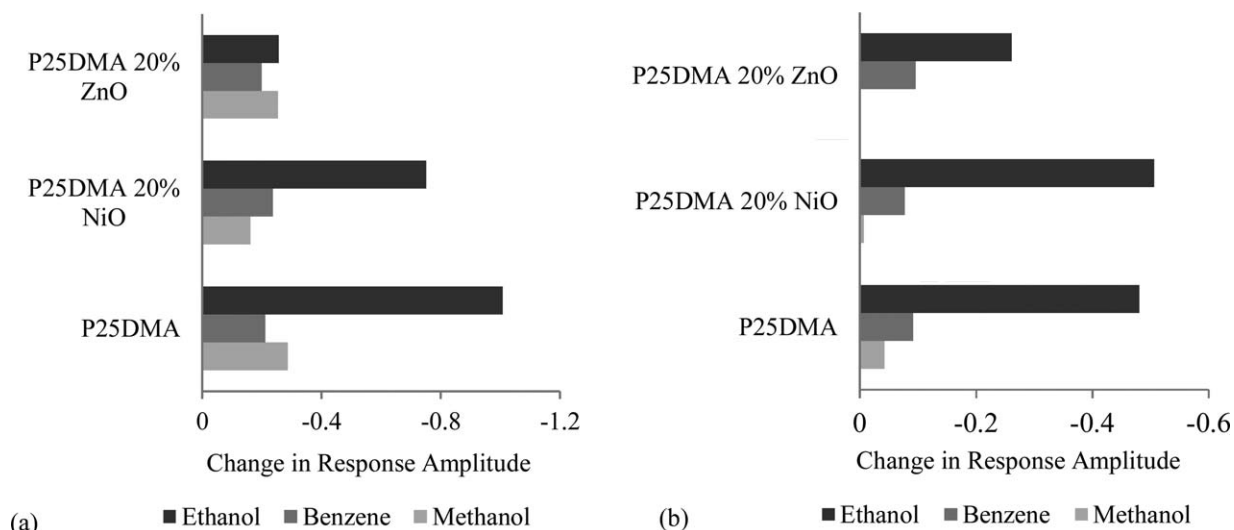
Figure 6. The change in resonant frequency amplitude (unitless) measured at steady-state for different analytes at (a) 5000 ppm and (b) 625 ppm for each sensing material.

High selectivity is also needed. Selectivity aspects are discussed in the following section.

Selectivity

Selectivity toward ethanol was measured by exposing the sensing materials to ethanol and two typical interferent gases (benzene and methanol). These two interferents were chosen to show proof of concept (for instance, the effect of humidity is beyond the scope of this article). The change in response amplitude was measured for three different analytes, for each sensing material. The gases were tested individually at four different concentrations (5000, 2500, 1250, and 625 ppm) and similar trends were seen at all four concentrations. Representative results are shown in Figure 6(a,b) for 5000 and 625 ppm, respectively, i.e., at the two extremes of the concentration range. The response (change in response amplitude) for each gas is graphically displayed. The target analyte's response (ethanol, in this case) was much larger than the response to the interferents, thus indicating a highly selective

sensor. This was the case for both P25DMA and P25DMA 20% NiO.

Selectivity of the sensing materials was compared based on the same concentration of gas tested. At 5000 ppm, ethanol, benzene, and methanol had very similar responses for P25DMA 20% ZnO, which was due to the analytes saturating P25DMA 20% ZnO. However, at 625 ppm, P25DMA 20% ZnO's response was approximately twice as large for ethanol. Once saturation has been reached, the change in response amplitude will not increase, despite an increase in analyte concentration. Saturation of ethanol can be seen in Figure 5.

For P25DMA 20% NiO and P25DMA, similar trends were seen in Figure 6 at both 5000 and 625 ppm, since saturation was much less of an issue. Both P25DMA 20% NiO and P25DMA produced a much higher response to ethanol, than the other two interferents, when exposed to the same concentration of each gas.

When it comes to selectivity, many accepted values in the literature are around the value of 2; however, the higher the value of selectivity, the better.[15,16] Therefore, both P25DMA and P25DMA
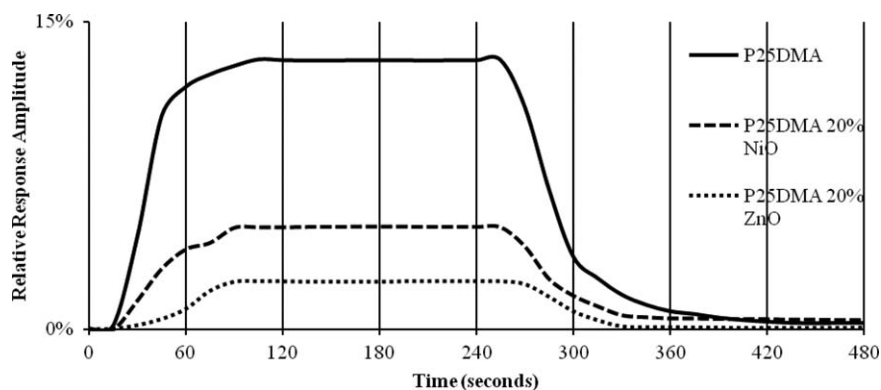
Figure 7. Response and recovery times for each sensing material measured for ethanol at 5000 ppm. Relative response amplitude is the percent change in the amplitude of the response from the baseline, when the sensing material is exposed to an analyte.

20% NiO, which had selectivity values between ethanol and benzene of 5.3 and 6.4, respectively (and even higher between ethanol and methanol), exhibited high selectivity toward ethanol since ethanol produced a much larger response than the interferents. P25DMA 20% ZnO, on the other hand, exhibited moderate selectivity at 625 ppm and poor selectivity at 5000 ppm.

Response/Recovery Time

The response and recovery times were measured at 5000 ppm of ethanol, since 5000 ppm produced the largest response signal. Generally, the larger the response, the slower the response and recovery times because the response time is measured at 90% of the full response and the recovery time is measured as 90% recovery with respect to the baseline (Figure 7). Therefore, the response and recovery times for lower concentrations should be shorter, thus making the tests at 5000 ppm essentially "worst case scenario" tests. The response and recovery times were 35 and 100 s for P25DMA, 60 and 70 s for P25DMA 20% NiO, and 60 and 60 s for P25DMA 20% ZnO. These response and recovery times are acceptable for a transdermal ethanol sensor and are of the same time scale as current breathalyzers[17]; however, these times could be improved in the future with improvements to the sensor such as optimization of sensing material thickness and sensor electronics (improvements that are beyond the scope of the current investigation).

CONCLUSIONS

Detailed evaluation of five different sensing materials using a very flexible test set-up for gas analytes, ultimately identified P25DMA and P25DMA 20% NiO as good sensing materials for ethanol with high selectivity and LoD of 3 and 24 ppm, respectively. P25DMA 20% ZnO had poor sensitivity and selectivity to ethanol; however, it may be useful in a sensing array application as a way to avoid false positives. Response and recovery times were all acceptable in the order of seconds.

ACKNOWLEDGMENTS

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