

Ionic liquid high temperature gas sensors

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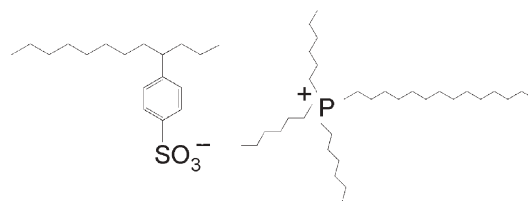
An ionic liquid piezoelectric gas sensor was demonstrated for detection of polar and nonpolar organic vapors at high temperature with fast linear and reversible response.

Identifying and correcting emissions from high-polluting vehicles require small sensors working at high temperatures to monitor pollutants in exhaust gas or leaking fuels.^{1,2} High temperature gas sensing is conventionally achieved by using semi-conductive metal oxides, such as SnO₂ and TiO₂.^{3–5} The resistance of metal oxides changes in the presence of organic vapors, CO or H₂. It takes relatively a long time to reach equilibrium for the sorption of analytes from gas phase onto the metal oxides, especially for porous materials. The dependency of the resistance of the metal oxides on the vapor concentration is not linear, which reduce the accuracy of quantitative analysis.⁶ Some metal oxides work only at temperatures higher than a “switch on” value, *e.g.* >700 °C for SrTiO₃.^{7–9} Rubbery polymers with low glass transition temperatures (*T_g*) were used as coatings for detection of nonpolar or weakly polar organic vapors.¹⁰ The vapor sorption in rubbery polymer is reversible and attains equilibrium rapidly.^{10,11} However, the mechanical properties of rubbery polymers strongly depend on temperature.¹² Most polymer materials with low *T_g* are not stable at high temperature. Therefore, applications of polymer materials for high temperature vapors sensing are limited. Furthermore, if the vapors cannot adsorb on the materials, the large surface-area to volume ratio sensing materials, such as graphite¹¹ or oxides^{3–5} would not work for high temperature gas sensing.

Room-temperature ionic liquids (ILs) are a relatively new class of compounds containing organic cations and anions, which melt at or close to room temperature. ILs show great promises as gas sensing materials.¹³ ILs have negligible vapor pressure and many possess high thermal stability.¹⁴ Most ILs show typical decomposition temperatures of 350+ °C. The remarkable thermal stability has important implications in the use of ILs for high temperature gas sensing.

In this paper, we demonstrate an IL high temperature piezoelectric gas sensor using phosphonium dodecylbenzene-sulfonate (*i.e.* P_{6,6,6,14}DBS) as sensing material coated on quartz crystal microbalance (QCM) transducers. QCM is a mass sensor and has been used for organic vapor detection at room temperature.¹⁵ P_{6,6,6,14}DBS (Scheme 1) was prepared *via* an alcohol-to-alkyl halide conversion method,¹⁶ a simple one-pot synthesis.† TGA study shows it is thermal stable up to 350 °C, Fig. 1. Our studies show that this IL/QCM sensor has a fast and reversible response to various organic vapors at high temperature.

The P_{6,6,6,14}DBS was coated on the QCM from its ethanol solution. Typically, the surface loading of the IL was *ca.* 17 μg cm⁻²



Scheme 1 Structure of IL P_{6,6,6,14}DBS.

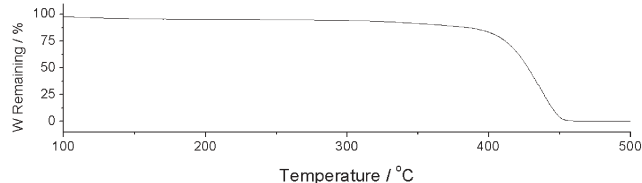


Fig. 1 TGA curve of P_{6,6,6,14}DBS.

in this work. Ultra thin films with thickness less than tens of nanometers are more rigid and will have little shear modulus change upon vapor sorption.^{10,17} The P_{6,6,6,14}DBS/QCM sensor for detecting of various organic vapors was studied at elevated temperatures controlled by a GC oven. The test vapors were diluted by the pure nitrogen carrier gas and the concentrations of the vapors were controlled by two mass-flow controllers (MKS Instruments, Inc.).

Shown in Fig. 2, upon exposure of P_{6,6,6,14}DBS/QCM sensor to both polar (ethanol or dichloromethane) and nonpolar (heptane or benzene) organic vapors, a decrease of the resonance frequency of the QCM was observed over a range from room temperature to as high as 200 °C. At bare QCM, the frequency shift was very small. As expected by thermodynamics, the frequency change decreased exponentially with increasing temperature. P_{6,6,6,14}DBS is polar, consequently, bigger sensitivity was observed for ethanol and dichloromethane than that of heptane and benzene at all temperatures. Table 1 shows the data summary for both P_{6,6,6,14}DBS/QCM and the bare QCM response to 110 mg L⁻¹ ethanol vapor at elevated temperatures. Not only does the IL/QCM show a higher sensitivity at all temperatures than the bare QCM, but also these data illustrate that the IL/QCM can be used as a gas sensing device at high temperatures. When the system was cooled down to 24 °C, the IL/QCM sensor gave reproducible response at 24 °C again indicating high stability and reversibility. At temperature much higher than the boiling point, very few vapor molecules can be adsorbed on solid surfaces. Consequently, we can regenerate the sensors by raising the temperature to desorb other impurities without affecting the IL film. We also studied the ionic

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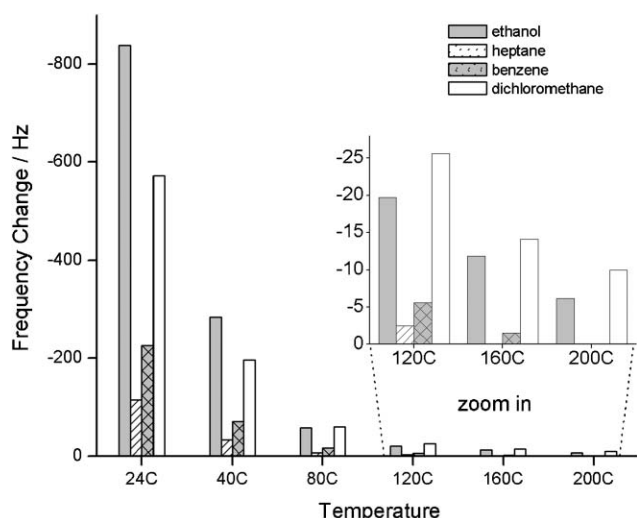


Fig. 2 Frequency change of the IL/QCM sensor exposed to ethanol, heptane, benzene and dichloromethane at various temperatures. The same concentration was used for the vapors at all temperatures.

Table 1 Frequency change (Hz) when bare QCM and IL/QCM exposed to N_2 flow containing 110 mg L^{-1} ethanol vapor

$T/^\circ\text{C}$	24	40	80	120	160	200
On Bare QCM	36	10.4	3.9	1.4	—	—
On QCM/IL	836	284	57.4	19.7	11.9	6.2

liquid film thickness effect. When IL films thickness is between $0\text{--}25 \mu\text{g cm}^{-2}$, the frequency change increased linearly with the film thickness. However, increased frequency change was not observed at larger IL thickness than $25 \mu\text{g cm}^{-2}$.

Shown in Fig. 3a, linear relationship of the frequency changes and the concentrations of vapor were obtained over the 0% to 100% saturation vapor pressure range at 120°C for all four organic vapors tested. (Note: 100% is when the N_2 flow was saturated with the sample vapor at 24°C , the other percentage is obtained by dilution using the second pure N_2 flow.) The detection limit could reach as low as 5%, which equals to 7 mg L^{-1} , ethanol, 12 mg L^{-1} , heptane, 21 mg L^{-1} , benzene and 100 mg L^{-1} , dichloromethane. Fig. 3b is the sensorgram of benzene at 120°C showing excellent reversibility of the absorption/desorption processes. This characteristic eliminates the need to purge the system to regenerate the sensing sites before each measurement, which assure a real-time monitoring. Each time the sample channel was switched on or off, a constant frequency was established in a few minutes. Since a very slow flow rate of the carrier gas 30 ml min^{-1} was used to minimize the mechanical vibration of the QCM, it took several minutes to fill or purge off the sensor chamber, which is *ca.* 150 ml in volume. So the time to reach constant frequency is not the equilibrium time of absorption or desorption. It was found that the solubility equilibrium of organic vapors in ILs could be reached in a few seconds.¹⁸ The response time and the sensitivity depend also on the boiling point of the organic samples.¹⁹ When the flow rate was increased, the response time decreased, while the frequency change did not depend on the flow rate.

Several factors may cause the frequency change of the QCM upon absorption of organic vapors into IL film. At an ideal

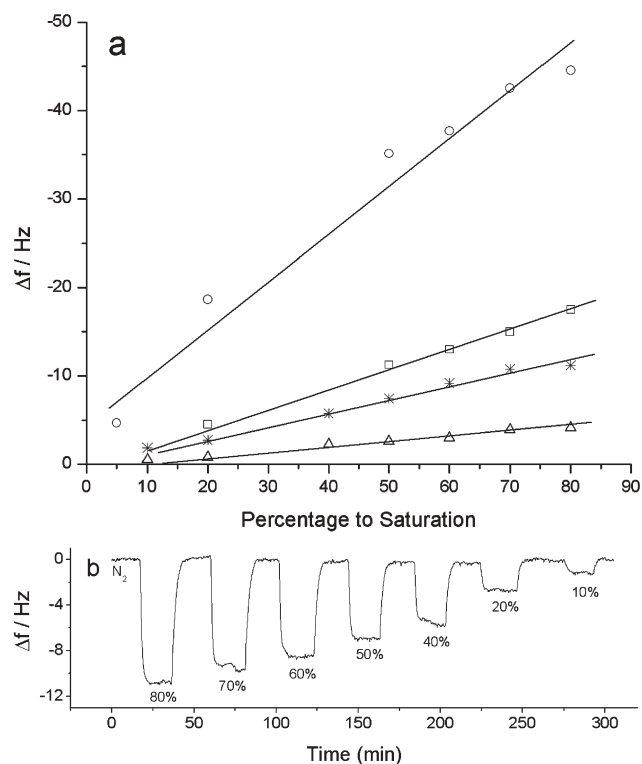


Fig. 3 (a) Frequency change vs. concentration of the IL/QCM sensor exposed to ethanol (square), heptane (triangle), benzene (star) and dichloromethane (circle) at 120°C ; (b) sensorgram of benzene at 120°C from various concentrations.

condition, the frequency change is only caused by the mass loading on the surface. To evaluate mass loading effects experimentally, an equation was derived, from the Sauerbrey equation,¹⁵ relating sensor responses to partition coefficients: $\Delta f_{\text{v(mass)}} = \Delta f_{\text{n}} C_{\text{v}} K / \rho$, where $\Delta f_{\text{v(mass)}}$, Δf_{n} , C_{v} , K and ρ are, respectively, the frequency shift caused by the adsorption of the vapor, the coating thickness in kHz, the vapor concentration in the gas phase, the partition coefficient and the coating material's density. However, reports show that both the mass loading and the viscosity change of the IL film upon the absorption of vapors can cause the frequency change at room temperatures.¹⁸ The change of the viscosity or modulus of the coating is reflected by the change of damping resistance fitted by the BVD circuit.²⁰ We measured simultaneously the damping resistance and the frequency change during the vapor detection experiments using Maxtek RQCM. Table 2 summarized the data of damping resistance (R) and its change ($\Delta R\%$) for the four samples at different temperatures. At room temperature, the $\Delta R\%$ values are relatively large, *e.g.* 11% for ethanol and 12% for dichloromethane, indicating a big viscosity change of the film upon the absorption of organic vapors. This agrees with the previous report at room temperature.¹⁸ However, at higher temperature, the $\Delta R\%$ values decreased. At 120°C , it is less than 2.6% for the four samples tested due to the smaller amount of vapors absorbed in the IL film at high temperature. Consequently, the change of viscosity caused by the gas adsorption on the IL film is very small at high temperature, and hence, the frequency changes were contributed mainly from the mass loading in the IL film and the Sauerbrey equation relating frequency change to pure mass

Table 2 Value of damping resistances and their changes during experiments

	24 °C		40 °C		80 °C		120 °C	
	R (Ω)	ΔR%	R (Ω)	ΔR%	R (Ω)	ΔR%	R (Ω)	ΔR%
Ethanol	4.7	± 11%	3.9	± 2.6%	4.0	± 1.9%	4.4	± 0.7
Benzene	3.3	± 3.7%	3.4	± 2.2%	3.4	± 1.1%	3.6	± 1.4%
Heptane	3.2	± 1.6%	3.1	± 1.3%	3.2	± 1.2%	3.4	± 1.5%
Dichloromethane	3.5	± 12%	3.5	± 7.1%	3.6	± 3.3%	3.9	± 2.6%

loading is valid. At high temperature, the Δf vs. C curve also mirrors the Henry's gas law²¹ (i.e., the concentration of a gas sample in liquid solvent is proportional to the concentration (or the partial pressure) of the sample in gas phase). Consequently, Henry constants can be measured with good accuracy at high temperature by IL/QCM sensors. The Henry constants of the four samples in IL P_{6,6,6,14}DBS at 120 °C were calculated to be 3.49×10^5 Pa, ethanol, 1.52×10^4 Pa, benzene, 1.95×10^6 Pa, dichloromethane and 2.01×10^6 Pa, heptane according to equation $p_i = C_i m_i$, where p_i is the partial pressure of the samples in gas phase, C_i is the Henry constant and m_i is the molar fraction of the samples in IL. Saturated vapor pressures were obtained from vapor pressure data.²² m_i was calculated from Sauerbrey equation (for 10 MHz crystal, the sensitivity is $1.02 \text{ ng cm}^{-2} \text{ Hz}^{-1}$) and the total weight of the IL film is $17 \mu\text{g cm}^{-2}$.

In conclusion, an ionic liquid piezoelectric gas sensor was demonstrated for detection of polar and nonpolar organic vapors at high temperature. The sensor gives linear, fast and reversible response at temperatures up to 200 °C. In particular, at high temperatures, the sensor response to the partial pressure of the gas sample is linear and abides by the Sauerbrey equation. Ionic liquids offer many options for chemical modifications and hence a huge flexibility in tailoring molecular recognition sites by controlled organic synthesis and surface designs. This provides an exciting opportunity to explore their application not only in high temperature gas sensing but also in highly sensitive and selective detection for trace analytes using IL sensor array.

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Notes and references

† Structural data of P_{6,6,6,14}DBS: Proton NMR (in CDCl₃, Hz) 7.86 (d, 2H, 8 Hz), 7.07 (dd, 2H, 8 Hz), 2.62 (tt, 1H, 5 Hz), 2.28 (m, 8H), 1.46 (m,

20H), 1.23 (m, 40H), 0.85 (m, 16H), 0.8 (t, 3H, 5 Hz), 0.75 (t, 3H, 5 Hz). ES-MS: anion $m/z = 325.18$ (calcd 325.49), cation $m/z = 483.4$ (calcd 483.86). FTIR (cm⁻¹): 2956, 2929, 2860, 1668, 1597, 1464, 1376, 1205, 1035, 1010, 832.

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