

# Surface Acoustic Wave Oxygen Sensor

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A surface acoustic wave (SAW) device that responds to oxygen pressure was developed by coating a 158-MHz quartz SAW device with an oxygen-binding agent. Two types of coatings were used. One type was prepared by dissolving an oxygen-binding agent in a toluene solution of a copolymer containing the axial ligand. A second type was prepared with an oxygen-binding porphyrin in a toluene solution containing excess axial ligand without a polymer matrix. In the polymer-based coatings, the copolymer served to provide the axial ligand to the oxygen-binding agent and as a coating matrix on the surface of the SAW device. The oxygen-sensing SAW device has been shown to bind oxygen following a Langmuir isotherm and may be used to measure the equilibrium constant of the oxygen-binding compound in the coating matrix.

The theory and applications of surface elastic waves (SAW) have been thoroughly reviewed by Richard M. White.<sup>1</sup> Since the publication of the work by Wohltjen and Dessy,<sup>2</sup> considerable interest in the use of SAW probes for chemical sensing has developed, and a review has been written by Ballantine and Wohltjen.<sup>3</sup> A good introduction to the theory and operation of SAW devices has been given by Wohltjen.<sup>4</sup> A review by Guilbault gives many applications of piezoelectric devices for chemical sensing.<sup>5</sup> An excellent review by Grate et al. gives a clear overview and comparison of the different acoustic wave sensors and methodology.<sup>6,7</sup> We are interested in developing a SAW air pressure sensor with sufficient sensitivity to measure pressure in the millitorr region. Previous research efforts to develop SAW pressure sensors have been based on the physical effect of pressure on a membrane of piezoelectric material. These types of SAW pressure sensors have limited sensitivity and are not suitable for pressure measurement below about 50 Torr. Rokhlin et al. have reviewed the various SAW pressure sensors that have been published.<sup>8</sup> The Lamb wave sensors, as reported by White, show the greatest promise for direct pressure measurements

at the millitorr level.<sup>9,10</sup> However, additional design and testing of a physical pressure sensor based on a Lamb wave device is needed. A SAW sensor responds to mass loading of the device surface. SAW chemical sensors are based on the frequency decrease which accompanies the absorption of an analyte species. The measurement of pressure by means of a chemically selective SAW sensor offers the potential for selectivity and variable sensitivity, since both the nature and the binding constant of the coating may be appropriately chosen. An enormous body of research on oxygen carriers already exists,<sup>11</sup> forming the basis for formulating a reversible oxygen-binding coating for a SAW device. An oxygen sensing SAW device could be used as an air-pressure sensor or an oxygen monitor.

Much of the research on oxygen binding agents has centered on efforts to develop synthetic oxygen carriers for applications ranging from synthetic blood to oxygen enrichment of air. There are numerous reviews on the subject.<sup>11-13</sup> The requirements of an oxygen-absorbing coating on a SAW device for oxygen sensing are essentially the same as those needed for a synthetic oxygen carrier. They are as follows:

(1) The compound should have the appropriate equilibrium constant for the reaction: binding agent + O<sub>2</sub> = binding agent-O<sub>2</sub>.

(2) Oxygen binding should be reversible and rapid. The mole ratio of oxygen to adsorber should be a function of the partial pressure of the oxygen in the system.

(3) The compound must be stable and not undergo oxidation. (Achieving this has been the major hurdle in the development of synthetic oxygen carriers. Oxygen tends to oxidize the central metal ion of the carrier or the carrier itself.)

(4) The compound must be amenable to coating or bonding onto the surface of the SAW device.

Nishide et al. reported the preparation of poly(alkyl methacrylate) copolymer membranes containing stable, reversible oxygen-binding agents.<sup>14,15</sup> The oxygen-binding

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(13) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* 1979, 79 (2), 139-179.

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agents were stabilized through bonding to an imidazole or pyridine group in the copolymer. They cast membranes of the metal complex/copolymer from toluene or chloroform solution for gas permeability studies. A solution of such a copolymer/oxygen binding agent could be used to spray-coat a SAW device with a film that would absorb oxygen selectively and reversibly.

Although SAW devices respond to mass loading of the device surface, which is the basis for their use as chemical sensors, other variables affect the frequency of the device. It is well known that SAW devices are sensitive to temperature changes.<sup>4</sup> Changes in the properties of polymer coatings, which are frequently used to facilitate analyte absorption and selectivity, can have a profound effect on the frequency of the SAW device. Bartley and Dominguez presented a theoretical treatment of changes in coating elasticity on the SAW device frequency and presented some experimental data.<sup>16</sup> Grate et al. showed that polymer-phase swelling associated with analyte absorption makes a significant contribution to the response of polymer-coated SAW sensors and can cause a larger contribution to frequency change than the gravimetric response.<sup>17</sup> A review of these effects is given in the recent report by Grate et al.<sup>7</sup>

In developing the theoretical response of the SAW device to oxygen adsorption, only the mass loading response is considered. The simplified relationship between SAW frequency change and mass is given by

$$\Delta f = (k_1 + k_2)f^2(m/A) \quad (1)$$

where  $\Delta f$  is the SAW resonance frequency change (Hz),  $k_1 = -9.33 \times 10^{-8} \text{ m}^2 \text{ s kg}^{-1}$ ,  $k_2 = -4.16 \times 10^{-8} \text{ m}^2 \text{ s kg}^{-1}$  for YX quartz oscillator,  $f$  is the SAW device resonance frequency (Hz),  $m$  is the mass of the coating (kg), and  $A$  is the coated area ( $\text{m}^2$ ). If the oxygen-binding sites on the coated area of the SAW device behave independently of the polymer matrix and if the solubility of oxygen in the polymer is neglected, then the binding of oxygen would be expected to follow a Langmuir-type equilibrium. Under such conditions the fraction of sites with oxygen molecules bound,  $\theta$ , is given by

$$\theta = \frac{P_{\text{O}_2}}{P_{1/2\text{O}_2} + P_{\text{O}_2}} \quad (2)$$

where  $P_{\text{O}_2}$  is the partial pressure of oxygen (Torr) and  $P_{1/2\text{O}_2}$  is the partial pressure of oxygen when one-half of the binding sites are occupied. This is a measure of the oxygen-binding constant where

$$1/K_{\text{eq}} = P_{1/2\text{O}_2}$$

The mass of oxygen bound to the active sites,  $m$  (kg), is given by

(15) Nishide, H.; Kawakami, H.; Toda, S.; Tsuchida, E.; Kamiya, Y. *Macromolecules* 1991, 24, 5851-5855.

(16) Bartley, D. L.; Dominguez, D. D. *Anal. Chem.* 1990, 62, 1649-1656.

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$$m = \theta nM \quad (3)$$

$$m = \frac{nMP_{\text{O}_2}}{P_{1/2\text{O}_2} + P_{\text{O}_2}} \quad (4)$$

where  $n$  is moles of binding sites and  $M$  is molecular weight of oxygen (kg/mol). By substituting eq 4 for  $m$  in eq 1, it may be readily shown that

$$\frac{1}{\Delta f} = \frac{A}{(k_1 + k_2)f^2nM} (P_{1/2\text{O}_2})(1/P_{\text{O}_2}) + \frac{A}{(k_1 + k_2)f^2nM} \quad (5)$$

Thus a plot of  $1/\Delta f$  vs  $1/P_{\text{O}_2}$  yields a straight line with an intercept equal to

$$\frac{A}{(k_1 + k_2)f^2nM} \quad (6)$$

and a slope equal to

$$\frac{A}{(k_1 + k_2)f^2nM} P_{1/2\text{O}_2} \quad (7)$$

For a particular coated SAW device, all the terms in eq 6 are constant. The oxygen-binding constant may then be calculated by dividing the slope by the intercept:

$$P_{1/2\text{O}_2} = \text{slope/intercept} \quad (8)$$

In the case where there is significant solubility of oxygen in the polymer matrix of the film, the dissolved oxygen will contribute to the mass of oxygen in the SAW device coating. This contribution is expressed from Henry's law:

$$C_{\text{O}_2} = k_d P_{\text{O}_2} \quad (9)$$

where  $C_{\text{O}_2}$  is the concentration of oxygen in the coating ( $\text{mol}/\text{m}^3$ ),  $k_d$  is the Henry's law solubility constant ( $\text{mol of O}_2/\text{m}^3$  Torr), and  $P_{\text{O}_2}$  is the partial pressure of oxygen (Torr). The mass of oxygen in the coating would then be given by the sum of the dissolved oxygen and the bound oxygen:

$$m = k_d P_{\text{O}_2} VM + \frac{nMP_{\text{O}_2}}{P_{1/2\text{O}_2} + P_{\text{O}_2}} \quad (10)$$

where  $V$  is the volume of the coating on the SAW device active area ( $\text{m}^3$ ).

Substituting eq 9 for  $m$  in eq 1 and rearranging yields

$$\frac{1}{\Delta f} = \frac{A}{BP_{1/2\text{O}_2}k_dVM + BnM + Bk_dVMP_{\text{O}_2}} (P_{1/2\text{O}_2})(1/P_{\text{O}_2}) + \frac{A}{BP_{1/2\text{O}_2}k_dVM + BnM + Bk_dVMP_{\text{O}_2}} \quad (11)$$

where  $B = (k_1 + k_2)f^2$ .

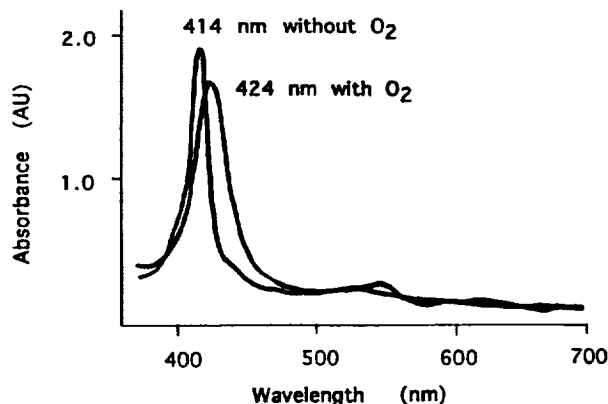
When  $k_d \ll P_{1/2O_2}$ , the terms in eq 10 containing  $k_d$  become negligible, and eq 10 reduces to eq 5. If  $k_d$  is large relative to  $P_{1/2O_2}$ , a plot of  $1/\Delta f$  vs  $1/P_{O_2}$  is not a straight line, and the intercept is oxygen-pressure dependent.

## EXPERIMENTAL SECTION

The toluene was HPLC grade. The (*N,N'*-disalicylide-neethylenediamine)cobalt(II) (CoS) was synthesized according to the procedure given by Bailes and Calvin.<sup>18</sup> The cobalt(II) picket-fence porphyrin (Co<sup>II</sup>PFP) was synthesized by Porphyrin Products, Logan, UT.<sup>19</sup> The cobalt(II) picnic-basket porphyrins were synthesized at Stanford University, Department of Chemistry.<sup>20,21</sup> Metalation of the picnic-basket porphyrins was done as follows. The entire procedure was performed in a N<sub>2</sub> atmosphere having an oxygen concentration of less than 1 ppm. A 50-mL round-bottom flask with a stir bar was charged with 25 mL of tetrahydrofuran (THF), 30 drops of 2,6-lutidine, and 40 mg of the picnic-basket porphyrin. The flask was fitted with a Vigreux column and brought to reflux. A 250-mg quantity of CoCl<sub>2</sub> was then added, and the reaction was refluxed for 10 h. The solvent was then removed by vacuum at room temperature. The solid residue was dissolved in 1:10 THF:benzene and loaded on a neutral alumina column. A single band was eluted with 1:10 THF:methanol:benzene. All of the unreacted CoCl<sub>2</sub> stayed in a plug at the top of the column. The solvent was pumped off the eluted band at room temperature, and the mass of the product was determined. Five molar equivalents of 1,5-dicyclohexylimidazole (DCHI) and enough toluene were added to make a coating solution containing the desired concentration of dissolved solids.

The oxygen-binding activity of the resulting solution was checked as follows. One drop of the solution used to coat a SAW device was dissolved in 2 mL of toluene in an inert atmosphere box maintained at or below 1 ppm O<sub>2</sub>. The resulting solution was placed in a cuvette, which was sealed and removed from the box. A UV-visible spectrum of the solution was obtained on a Hewlett Packard 8452A diode array spectrophotometer. O<sub>2</sub> was introduced into the cuvette by syringe, and a second spectrum was taken. The peak resulting from the O<sub>2</sub>-free solution is at a different wavelength than that obtained from the solution containing O<sub>2</sub>. For CoC<sub>1/2</sub>PBP with 1,5-DCHI, the peaks appear at 414 and 424 nm, respectively (see Figure 1). Upon purging the O<sub>2</sub>-saturated solution with Ar, the peak at 414 nm is restored, indicating a reversible O<sub>2</sub>-porphyrin adduct.

Poly(octyl methacrylate-*co*-vinylpyridine) (POM-*co*-VP) and poly(butyl methacrylate-*co*-vinylimidazole) (PBM-*co*-VI) were synthesized by radical copolymerization of octyl methacrylate or butyl methacrylate and freshly distilled 4-vinylpyridine or 1-vinylimidazole using azobis(isobutyronitrile) (VAZO-64) as an initiator. A toluene solution of the polymer was prepared and deaerated with nitrogen, and the desired weight of the oxygen-binding agent was added to the



**Figure 1.** UV-visible spectrum of CoC<sub>1/2</sub> picnic-basket porphyrin with 1,5-dicyclohexylimidazole in toluene. The peak at 414 nm corresponds to the oxygen-free solution while the peak at 424 nm corresponds to the oxygenated sample.

solution under a nitrogen atmosphere in a Schlenk-type storage tube. The glass transition temperature of the oxygen-binding polymers was not measured. Nishide et al. give a glass transition temperature of -8.0 °C for 2.5% CoS in poly(octyl methacrylate-*co*-4-vinylpyridine) and 78 °C for 37% cobalt-(II) picket-fence porphyrin in poly(octyl methacrylate-*co*-vinylpyridine).<sup>14,15</sup>

The frequency shift data were collected using a Model CEM-158-B (Microsystems, Inc.) frequency readout system and 158-MHz SAW devices. The frequency-readout module unit consisted of a radio frequency (rf) drive electronics circuit board that can detect the frequency output of two independent 158-MHz SAW oscillators. The frequency output from the readout electronics package was measured with a Fluke 7220A frequency counter. One of the two sensors was left uncoated and used as a "reference" sensor. The other sensor was coated with a chemically selective film and used as the "sample" sensor. The difference between the resonant frequencies of the reference and sample devices was measured. Measuring the difference frequency partially cancels out most frequency deviations caused by mechanical stresses and temperature fluctuations that the sensors experience. However, we have found that each device has different responses to temperature and pressure so that true cancellation does not occur. Since the difference amplifier did not show the sign relationship between the working device and the reference device, the actual frequency of each device was recorded. The difference was then calculated using the following relationship: frequency change,  $\Delta f = (f_{\text{ref}} - f_{\text{sam}})_{\text{initial}} - (f_{\text{ref}} - f_{\text{sam}})$ .

The SAW devices were spray-coated using a nitrogen-fed airbrush inside a glovebox under a nitrogen atmosphere. The sensor film loading was monitored during the spraying process by measuring the frequency shift. A separate CEM-158-B system inside the glovebox with the frequency counter located outside the glovebox was used. The sensor was spray-coated to produce a frequency drop of 300–500 kHz after complete evaporation of the solvent. Once the coating was applied to the sensor, the lid was glued onto the sensor with epoxy cement while the sensor was still in a nitrogen environment. Dual-tubulated nickel-plated sensor lids connected the two sensors in series. Each sensor was then influenced by the same pressure and gas species. The epoxy used was Hardman Epoxies 04001,

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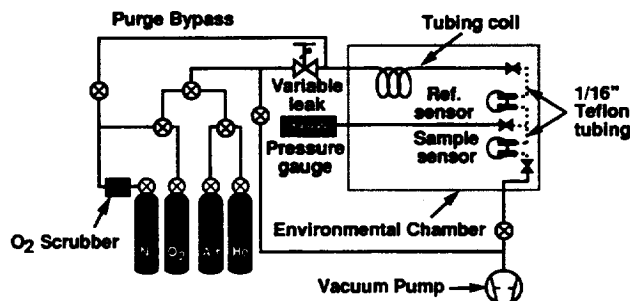


Figure 2. Schematic diagram of gas flow and pressure measurement system.

which is a fast-setting epoxy. This type of epoxy becomes soft at 150 °C, allowing removal and reuse of the lids by applying heat. Once the sensor was coated and the lid attached in the glovebox, the device was transferred to the pressure measurement system.

The coating was cured after the device was connected to the measurement system. It was found that the response of the device improved if the coating was cured at 60 °C for about 1 h under a positive nitrogen purge. This allowed for residual solvent to be driven out of the coating.

Figure 2 shows the gas and pressure control setup. The SAW devices and electronics module of the frequency measurement system were located inside a Delta Design, Model 3900 constant temperature chamber that allowed for control of temperature to  $\pm 0.1$  °C. The temperature inside the chamber was monitored using four 30 gauge, type T thermocouples. Two were used to monitor different locations within the chamber, and third was attached to the frequency readout board near the power supply section of the board. The fourth thermocouple was attached to the underside of the sample sensor. All data were recorded at 25 °C as measured by the sample sensor thermocouple.

For a typical run, the temperature of the chamber was first stabilized. The sensor and connecting tubing were then evacuated. The pressure of the selected test gas was slowly increased to specific points using the variable leak valve. Once the pressure stabilized at a particular value, frequency measurements were taken from each sensor. After measuring the response to oxygen, the system was evacuated and its response to nitrogen was determined. An oxygen scrubber was placed in the nitrogen line to ensure that no oxygen was present. A coil of copper tubing was inserted in the gas line preceding the sensors and within the chamber to allow the temperature of the test gas to equilibrate to that of the chamber.

## RESULTS AND DISCUSSION

For a SAW device coated with an oxygen-binding agent, the contribution to mass change when exposed to oxygen pressure is primarily given by eq 4, the Langmuir-type adsorption. Calculating the frequency change for different values of oxygen pressure using eqs 1 and 4 results in the curve shown in Figure 3a. This plot illustrates that as the binding sites become saturated the sensitivity to pressure change decreases. (The curve begins to flatten out). Thus, for a given pressure range there is an optimum binding constant for the active ingredient of the coating. Table 1 gives the optimum values of  $P_{1/2}$  for different oxygen (and air) pressure

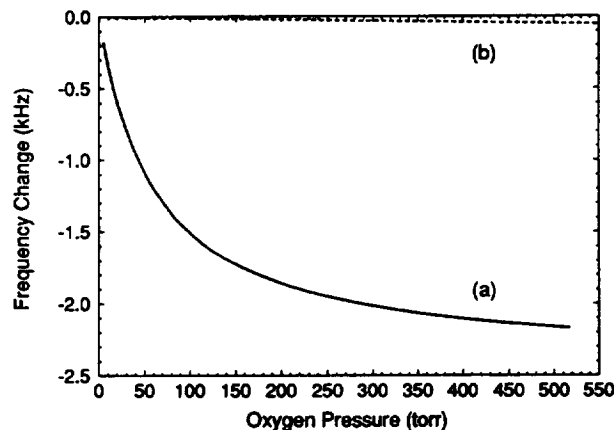


Figure 3. (a) Calculated plot of frequency change vs oxygen pressure of a 158-MHz SAW device coated with 10% CoPFP in a polymethacrylate. The following conditions were assumed: device area =  $1.6 \times 10^{-5}$  m<sup>2</sup>, coating density = 1.2 g/mL, coating thickness = 0.2  $\mu$ m, and  $P_{1/2} = 61$ . (b) Theoretical contribution from Henry's law.

Table 1. Optimum Binding Constants for Oxygen-Binding SAW Device Coatings\*

oxygen pressure range (Torr)	air pressure range (Torr)	binding constant, $P_{1/2}$ (Torr)
0.02–2	0.1–10	0.86
0.1–10	0.5–50	4.3
1.0–100	5.0–500	43
5.0–400	25–2000	214
10–1000	50–5000	430
20–2000	100–10,000	860

\* Values are based on the pressure needed to cause a minimum signal change  $10 \times 50$  Hz noise and a maximum pressure corresponding to 70% of the binding sites occupied.

ranges. The minimum pressure of each range is based on the pressure required to produce a signal change of 500 Hz, and the maximum pressure for each range is that required to saturate 70% of the binding sites.

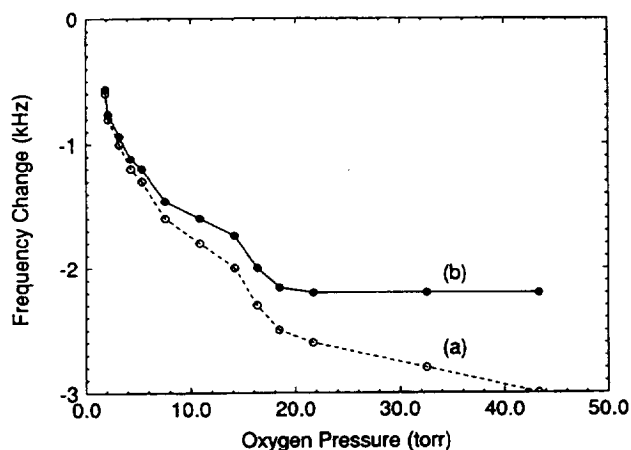
Line b of Figure 3 represents the contribution to frequency change due to the dissolution of oxygen in the coating, given by eq 9 (Henry's law contribution) based on a value of  $k_d = 1.0 \times 10^{-4}$  mL<sub>(STP)</sub>/mL Torr.<sup>22</sup> This value of  $k_d$  was measured by Nishide et al. for cobalt(II) picket-fence porphyrin/imidazole in poly(butyl methacrylate) at 25 °C. It is typical of the solubility of oxygen in methacrylates and is probably well within an order of magnitude of the value for the polymers used in this study.<sup>23</sup> This contribution to frequency change when the device is coated with an oxygen-binding agent is negligible.

It is well known that SAW devices have a frequency change response to pressure, even if there is no active coating on the device.<sup>2,24</sup> During our initial studies, we believed that the relative significance of the SAW device's response to the physical effects of pressure was negligible, and no correction was made for it. However, when the response of a coated device to helium or nitrogen was measured, it was found that a typical response (linear) was approximately 0.5–4 Hz/Torr, depending on the device. At higher pressures, this effect is

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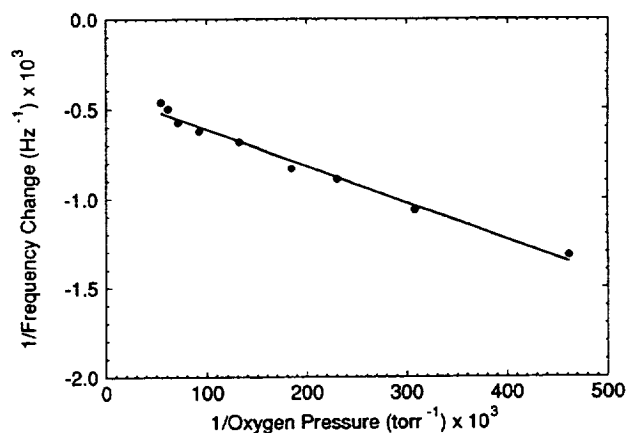
(24) Bowers, W. D.; Chuan, R. L. *Rev. Sci. Instrum.* 1989, 60 (7), 1297.



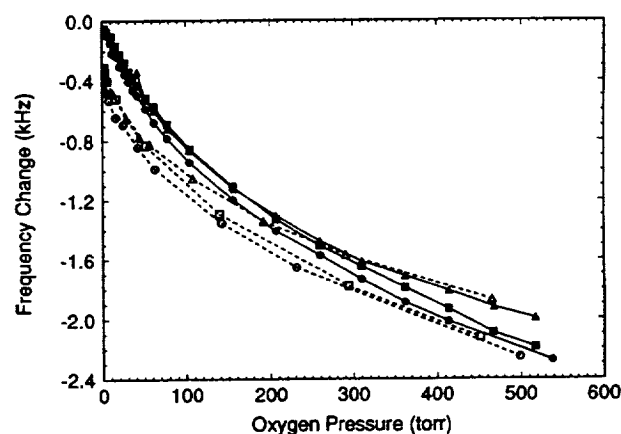
**Figure 4.** (a) Uncorrected oxygen pressure response curve for SAW device coated with CoS in PBM-co-VI. (b) Corrected for the physical effect of pressure on the SAW device.

significant relative to the frequency change caused by oxygen binding in coated devices. Also, at low pressures (1–50 Torr), the physical response to pressure was not always linear and sometimes caused anomalies in the low-pressure response curve shape for coated devices. With the exception of the data represented in Figure 6, the data have been corrected for the pressure response of the device to an inert gas. In the case of CoS, the correction was made using the response after CoS was saturated with oxygen. In later studies, the correction was based on data from the response of the particular device and coating to nitrogen.

CoS was chosen for our initial studies because it is easily synthesized. The frequency change vs the partial pressure of oxygen for a 158-MHz SAW device coated with CoS/poly-(butyl methacrylate-co-vinylimidazole) is shown in Figure 4a. After about 20 Torr, the response change became linear, which was characteristic of the response of an uncoated device to pressure or the response of a coated device to an inert gas. The slope of the response curve at higher pressures ( $3.87 \times 10^{-3}$  kHz/Torr) was determined, and a point-by-point correction to all frequency values was applied. The resulting corrected response curve is shown as Figure 4b. For the purpose of calculating the binding constant, a plot of  $1/\Delta f$  vs  $1/P_{O_2}$  was constructed using the data for pressures below 20 Torr oxygen pressure, as shown in Figure 5. The binding constant calculated from the slope and intercept is 5.0 Torr. The value reported by Nishide et al. is 23 Torr.<sup>14</sup> Note that the curves in Figure 4 change shape at an oxygen pressure of about 14 Torr. This was a reproducible phenomenon. It appears as if there was a change in the value of the binding constant. This could be due to a mixture of binding species in the coating, since CoS was not purified after the initial crystallization. If the Langmuir-type plot is based only on data for pressures below the point where this change in curve shape occurs, the resulting value for  $P_{1/2}$  is smaller (about 4.3 Torr). The CoS/polymer coatings were not stable, making it difficult to achieve reproducible results. The CoS in the coatings was quickly oxidized, and a coated device was no longer fully responsive after one pressurization cycle. It did not respond to oxygen at all after two pressurization/evacuation cycles.



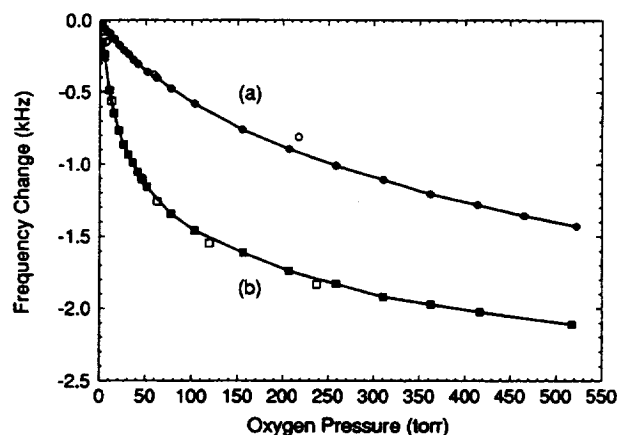
**Figure 5.** Langmuir-type plot for SAW device coated with CoS in PBM-co-VI: (intercept =  $-0.41 \times 10^{-3}$ , slope =  $-0.00204$ , correlation coefficient = 0.98,  $P_{1/2}$  = 5.0 torr.)



**Figure 6.** Oxygen pressure response curves for SAW device coated with Co(II)PFP in POM-co-VP. (—●—) run 1, increasing pressure; (---○---) run 1, decreasing pressure; (—■—) run 2, increasing pressure; (---□---) run 2, decreasing pressure; (—▲—) run 3, increasing pressure; (---△---) run 3, decreasing pressure.

The picket-fence porphyrins (PFP) have been reported to be quite stable to oxidation once the axial ligand site on the central metal atom is occupied and are ideal candidates for use as coatings for SAW oxygen sensors.<sup>15,19</sup> Plots of frequency decrease vs oxygen pressure for several pressure cycles using a 158-MHz SAW device coated with Co<sup>II</sup>PFP in POM-co-VP are shown in Figure 6. The toluene solution used to spray the device was prepared to contain 2% polymer and 1% Co<sup>II</sup>PFP, which provided a coating containing 34% CoP. Figure 6 represents three different pressurization/evacuation cycles on the same device, illustrating the degree of reproducibility. The hysteresis which may be noted in Figure 6 when cycling from high pressure back to low pressure is due to the slow diffusion of oxygen in the polymer matrix. The average binding constant calculated from the Langmuir-type plot of the data represented by Figure 6 is 266 Torr. The value reported by Nishide et al. is  $P_{1/2} \approx 340$  Torr.<sup>15</sup>

It was found that coatings containing high concentrations ( $\geq 30\%$ ) of Co<sup>II</sup>PFP were not as stable as coatings containing lower concentrations of Co<sup>II</sup>PFP ( $\leq 25\%$ ). However, high concentrations of the oxygen-binding agent in the coating were needed to achieve good signal to noise measurements. It is important to have a coating that will provide a large

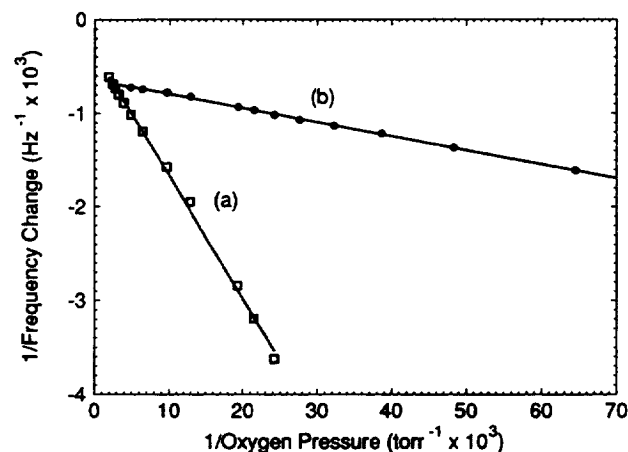


**Figure 7.** Oxygen pressure response curves for SAW devices coated with (a)  $\text{Co}^{\text{II}}\text{C}_{1/2}\text{PBP}$  in POM-co-VP and (b)  $\text{Co}^{\text{II}}\text{C}_{1/2}\text{PBP}/1,5\text{-DCHl}$ : (●) POM-co-VP, increasing pressure; (○) POM-co-VP, decreasing pressure; (■) 1,5-DCHl, increasing pressure; (□) 1,5-DCHl, decreasing pressure.

signal response relative to the background response. Although the porphyrins are excellent oxygen-binding agents, having good stability and a range of binding constants, they are massive molecules which cause high loadings of the SAW device. A 158-MHz device cannot be loaded with a coating that causes a frequency drop greater than about 300 kHz without risking overloading the device. Thus if the coating were 100% porphyrin, the maximum amount of porphyrin which could be coated onto the device would be about  $7 \times 10^{-8}$  mol. If every porphyrin unit were to bind an oxygen, the observed frequency shift would be about 960 kHz. A 960-kHz frequency decrease is more than enough to have a good signal to noise ratio, but only a fraction of this can be achieved in practice, since it is impossible to cover 100% of the device area with 100% porphyrin. Work is continuing on methods to maximize the sensitivity of the coating.

The picnic-basket porphyrins (PBP) are stable oxygen-binding compounds which offer greater flexibility in tailoring the binding constant to optimize a SAW coating for the pressure range to be measured.<sup>20,21</sup> In addition to the possibility of changing the central metal ion, the length of the bridge or "handle" can be changed to change the oxygen-binding constant. The bridging group of the PBP used in these studies consists of an  $-\text{OCH}_2-$  unit between the isophthalate rings, which are joined to the porphyrin ring by the amide linkages. This PBP is designated as  $\text{C}_{1/2}\text{PBP}$ . Figure 7a shows the response curve for a device coated with 20%  $\text{Co}^{\text{II}}\text{C}_{1/2}\text{PBP}$  in POM-co-VP. The value of  $P_{1/2}$ , as determined from a plot of  $1/\Delta f$  vs  $1/P$ , was found to be 368 Torr (see Figure 8a). This is considerably larger than the value of 7 Torr determined spectroscopically in toluene solution (unpublished data). However, the solid polymer matrix is very different, and a comparison cannot be made.

The shape of the response curve for all porphyrin-based coatings with a polymer matrix was distorted relative to the theoretical curve (Figure 3) and was consistently more linear than expected. This distortion was not observed in the case of CoS. The polymer matrix was used to provide the axial ligand to the oxygen-binding agent and to serve as a matrix for the coating. To check the effect of the polymer on the shape of the response curves, a device was prepared with a



**Figure 8.** Langmuir-type plots for data represented in Figure 7: (●)  $\text{Co}^{\text{II}}\text{C}_{1/2}\text{PBP}$  in 1,5-DCHl, (□)  $\text{Co}^{\text{II}}\text{C}_{1/2}\text{PBP}$  in POM-co-VP.

coating of  $\text{Co}^{\text{II}}\text{C}_{1/2}\text{PBP}$  and excess 1,5-dicyclohexylimidazole (3.7:1 ligand/porphyrin mol ratio) as the axial ligand. The response curve is shown in Figure 7b. Note that this curve is much closer to the expected shape shown in Figure 3.  $P_{1/2}$ , as determined from the corresponding plot of  $1/\Delta f$  vs  $1/P$ , was 23 Torr (see Figure 8b), much closer to the toluene solution value of 7 Torr. There are no values of  $P_{1/2}$  for the solid porphyrin/ligand with which to compare the 23 Torr value. It is not clear why the polymer matrix causes the curve shape to be so different in the case of porphyrin-binding agents. It appears to have the effect of decreasing the oxygen-binding constant. Polymer coatings can contribute significantly to the device response.<sup>7</sup> Polymer swelling causes an increase in response (larger frequency decrease), but significant swelling due to the solubility of oxygen in the polymer would not be expected. However, resonance effects can cause a smaller response, as was observed. It is not known how oxygen binding affects the elasticity of the porphyrin/polymer complex or whether or not oxygen binding induces film resonance effects.

Although the response curve of Figure 7b is very close to the theoretical curve of Figure 3, the total frequency decrease expected from the amount of porphyrin known to be present in the coating was not observed. Only 20–40% of the sites were active, depending on the coating thickness. Thinner coatings gave a higher fraction of active sites, indicating that at least part of the problem is due to incomplete oxygen penetration of the coating. Precautions were taken to make certain that the coating solution bound oxygen by running the absorption spectrum in the absence of oxygen and then in the presence of oxygen. The absorption maximum for the oxygenated form occurs at 6–10 nm longer wavelength. However, the percent activity of the coating solution before applying it to the device was not determined. Thus, some portion of the lowered activity in the final coating could have originated in the coating solution.

## CONCLUSION

Use of oxygen-binding porphyrins as coating materials for SAW devices gives a chemical sensor that can be used to measure oxygen partial pressure. Application of the SAW sensor to the measurement of binding constants for adsorbent-type coatings has also been demonstrated. Although we did

not characterize interferences, we would expect few interferences when the device is coated with porphyrin/ligand only. Carbon monoxide is known to bind to oxygen-binding porphyrins and would be an expected interference. If polymer-based coatings are used, then there could be numerous interferences due to the absorption of organic vapors by the polymer. Although coatings prepared from porphyrin/ligand only gave more ideal response, they were not as rugged as the ones involving a polymer matrix. More rugged polymer-free porphyrin coatings could probably be achieved by bonding the ligand to the quartz surface. We chose to control the oxygen partial pressure by controlling the total pressure because our initial investigation was aimed at developing a SAW air pressure sensor. This created the need to correct for the physical effect of pressure on the SAW device.

However, measurements of oxygen-binding constants could be done more conveniently by using nitrogen/oxygen standard mixtures at constant total pressure.

Problems with achieving response which is entirely due to oxygen binding still exist since the activity of the coatings was less than expected from the amount of porphyrin applied. With further development of coating techniques for achieving high response levels without the presence of interfering substances, the SAW oxygen sensor could be both a sensitive pressure device and a convenient method for measuring oxygen-binding constants. Elimination of the polymer matrix has been shown to bring us closer to this goal.

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