

Chemical Sensors Based Upon Inorganic Systems

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The field of chemical sensors is a rapidly growing area [1-10]. Chemical sensors themselves, however, have been around since the early 1900's: pH sensors were first reported in 1906, and simple pH electrodes have been known since 1935 [10]. The majority of growth in the area of sensing technology, though, has come only in the last thirty years. The recent growth of chemical sensors has not been a result of instrumental limitations, rather, it has been driven by the "fact that the chemical/instrument interface (i. e. the sensor) is today more commonly the limiting aspect of the chemical analysis capability" [11].

The role of inorganic chemistry in the development of chemical sensors has been quite substantial. Metal oxides have been used in numerous chemical sensors and were first reported by Seiyama [12]. Tin oxide (SnO_2) was utilized in one of the first commercially available gas sensors (Fig. 1) and is still used today. The principle of its operation relies upon the fact that SnO_2 is a n-type semiconductor. Upon interaction with a reducing gas, the resistance of the tin oxide decreases in an amount proportional to the gas concentration. Another metal oxide, stabilized zirconia, is used commercially in automobile oxygen sensors to maintain a proper air-to-fuel ratio [13]. This is important in terms of improving combustion and reducing emissions [14]. The zirconia sensor operates on the principle of ionic (O^{2-}) conduction. A difference in oxygen partial pressures on the inside and outside of the sensor produces an electromotive force which can be related to oxygen concentration in the exhaust [15].

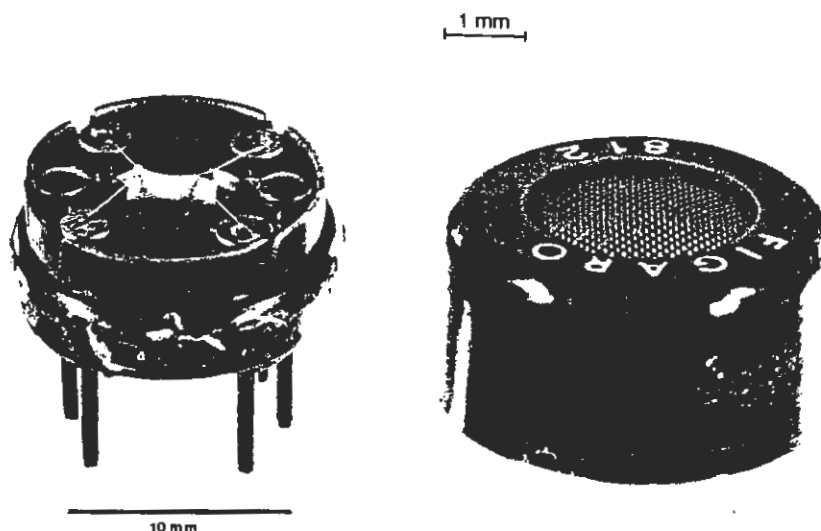


Figure 1. Figaro Corporation tin oxide gas sensor [13]

Recently, metal phthalocyanines have been used as sensing elements for several redox-active analytes. Metal phthalocyanines are well-suited for use in chemical sensors for a variety of reasons. They exhibit high chemical and thermal stability, can be synthesized in high yields, and exhibit interesting electrochemical and optical properties. Perhaps, the most widely studied chemical sensor containing a phthalocyanine is the lead phthalocyanine (PbPc) gas sensor [16,17]. This system has been primarily studied with respect to its interaction with nitrogen dioxide. The operating principle of the sensor is analogous to that of SnO_2

although its response is reversed due to the fact that PbPc is a p-type semiconductor. However, reproducibility in this system has proved elusive, and, thus, it has not been commercially implemented.

A residual aqueous chlorine sensor has recently been reported which utilized a lutetium bisphthalocyanine (LuPc_2) thin film as the sensing element [18]. The method used for the sensor involves coating a planar optical waveguide with the LuPc_2 thin film (fig. 2).

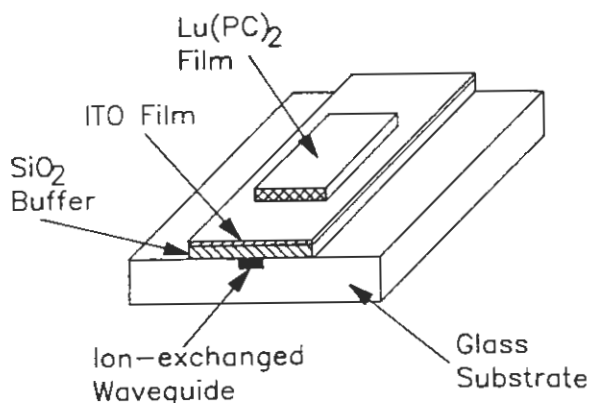


Figure 2. Schematic of optical waveguide [18]

The sensing principle of this system utilized the change in the LuPc_2 absorption spectrum upon oxidation by chlorine from LuPc_2^+ to LuPc_2^{2+} . The magnitude of the change produced in the spectrum can be related to the chlorine concentration of a sample.

Another recent article reported the use of cobalt phthalocyanine (CoPc) immobilized in a screen-printed carbon electrode as an amperometric sensor for the biologically important molecule glutathione [19]. CoPc was employed because it has been shown to reduce the overpotential for glutathione oxidation [20]. The reduction in overpotential and the use of glutathione peroxidase (which catalyzes the oxidation of glutathione in the body) conferred selectivity to the technique.

A third class of inorganic compounds which has been used as chemical sensors includes luminescent ruthenium and platinum pyridyl compounds. These compounds are of interest as oxygen sensors due to the quenching effect that oxygen has on their emission intensity. Inorganic luminescent compounds are superior to their organic counterparts due to greater stability, longer excited-state lifetimes, and larger Stokes shifts [21, 22].

A recent example of this type of sensor incorporated $[\text{Ru}(\text{bipy})_3]^{2+}$ and $[\text{Ru}(\text{ph}_2\text{phen})_3]^{2+}$ (bipy = 2,2'-bipyridine; ph_2phen = 4,7-diphenyl-1,10-phenanthroline) in a silica gel prepared by the sol-gel process [23]. The O_2 sensor was constructed by coating a clad optical fiber with this doped silica gel. A greater response to oxygen was observed with $[\text{Ru}(\text{ph}_2\text{phen})_3]^{2+}$, and the oxygen sensitivity of the probe was enhanced by varying the pH used in the sol-gel process.

Compounds of the type $\text{Pt}(\text{CN})_2(\text{L})$ (L = 4,7-diphenyl-1,10-phenanthroline; 4,4'-di-*t*-butyl-2,2'-bipyridine) have also been used as oxygen sensors [22]. These compounds were incorporated into a silicone polymer. These compounds exhibit greater sensitivity to oxygen than did the ruthenium complexes. The platinum complexes also displayed excimer emission with the location of the emission maximum dependent on the silicone microenvironment.

A complication in the implementation of these devices has been the fact that the excitation light source has traditionally been rather bulky. A recent article has described an all-solid-state device utilizing $[\text{Ru}(\text{bipy})_3]^{2+}$ as the luminescent complex [24]. The excitation source in this device is a new type of high-intensity blue light-emitting diode (LED). Blue LED's have traditionally been hard to produce, and those that have been used in sensors have suffered from low output intensity. Using this new diode, a significantly smaller oxygen sensor was designed and tested successfully.

References

1. Cammann, K; Lemke, U.; Rohen, A.; Sander, J.; Wilken, H.; Winter, B., "Chemical Sensors and Biosensors-Principles and Applications," *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 516-539.
2. Meyerhoff, M. E., "In Vivo Blood-Gas and Electrolyte Sensors: Progress and Challenges," *Trends Anal. Chem.* **1993**, *12*, 257-266.
3. Madou, M.; Tierney, M. J., "Required Technology Breakthroughs to Assume Widely Accepted Biosensors," *Appl. Biochem. Biotech.* **1993**, *41*, 109-128.
4. Janata, J., "Chemical Sensors," *Anal. Chem.* **1992**, *64*, 196R-219R.
5. *Fundamentals and Applications of Chemical Sensors*; Schuetzle, D.; Hammerle, R., Eds.; American Chemical Society Symposium Series 309; American Chemical Society: Washington, D. C. 1986.
6. *Biosensors and Chemical Sensors: Optimizing Performance Through Polymeric Materials*; Edelman, P. G.; Wang, J., Eds; American Chemical Society Symposium Series 487; American Chemical Society: Washington, D. C. **1992**.
7. *Biosensor Design and Application*; Matthewson, P. R.; Finley, J. W., Eds.; American Chemical Society Symposium Series 511; American Chemical Society: Washington, D. C. **1992**.
8. Janata, J. *Principles of Chemical Sensors*; Plenum: New York, 1989.
9. Madou, M. J. *Chemical Sensing with Solid-State Devices*, Academic Press: San Diego, 1989.
10. Buck, R. P., "Expanding Technology for Sensor Design and Fabrication," *Electrochim. Acta* **1991**, *36*, 243-251.
11. Murray, R. W. "Chemical Sensors and Microinstrumentation: An Overview," In *Chemical Sensors and Microinstrumentation*; Murray, R. W.; Dessy, R. E.; Heineman, W. R.; Janata, J.; Seitz, W. R., Eds.; American Chemical Society Symposium Series 403; American Chemical Society: Washington, D. C. 1989; 1-19.
12. Seiyama, T.; Kato, A.; Fujiishi, K.; Nagatani, M. "A New Detector for Gaseous Components Using Semiconductive Thin Films," *Anal. Chem.* **1962**, *34*, 1502-1503.
13. Moulson, A. J.; Herbert, J. M. *Electroceramics*, Chapman and Hall: London, 1990.

14. Sheppard, L. M. "Automotive Sensors Improve Driving Performance," *Am. Cer. Soc. Bull.* **1992**, *71*, 905-913.
15. Ketron, L. "Ceramic Sensors," *Am. Cer. Soc. Bull.* **1989**, *68*, 860-865.
16. Wright, J. D. "Gas Adsorption on Phthalocyanines and its Effects on Electrical Properties," *Prog. Surf. Sci.* **1989**, *31*, 1-60.
17. Bott, B. A. "A Highly Sensitive NO₂ Sensor Based on Electrical Conductivity Changes in Phthalocyanine Films," *Sens. Actuators* **1984**, *5*, 43-53.
18. Piraud, C.; Mwarania, E.; Wylangowski, G.; Wilkinson, J.; O'Dwyer, K.; Schiffrin, D. J. "Optoelectrochemical Thin-Film Chlorine Sensor Employing Evanescent Fields on Planar Optical Waveguides," *Anal. Chem.* **1992**, *64*, 651-655.
19. Wring, S. A.; Hart, J. P. "Chemically Modified, Screen-Printed Carbon Electrodes," *Analyst* **1992**, *117*, 1281-1286.
20. Halbert, M. K.; Baldwin, R. P. "Electrocatalytic and Analytical Response of Cobalt Phthalocyanine Containing Carbon Paste Electrodes toward Sulfhydryl Compounds," *Anal. Chem.* **1985**, *57*, 591-595.
21. Demas, J. N.; Degraff, B. A. "Design and Applications of Highly Luminescent Transition Metal Complexes," *Anal. Chem.* **1991**, *63*, 829A-837A.
22. Lee, W. W-S.; Wong, K-Y.; Li, X-M. "Luminescent Dicyanoplatinum(II) Complexes as Sensors for the Optical Measurement of Oxygen Concentrations," *Anal. Chem.* **1993**, *65*, 255-258.
23. MacCraith, B. D.; McDonagh, C. M.; O'Keefe, G.; Keyes, E. T.; Vos, J. G.; O'Kelly, B.; McGilp, J. F. "Fibre Optic Sensor Based on Fluorescence Quenching of Evanescent-wave Excited Ruthenium Complexes in Sol-Gel Derived Porous Coatings," *Analyst* **1993**, *118*, 385-388.
24. Hauser, P. C.; Tan, S. S. S. "All-Solid-State Instrument for Fluorescence-Based Fibre-Optic Chemical Sensors," *Analyst* **1993**, *118*, 991-995.