Optics Breathe New Life into Oxygen Sensing: Sol-Gel Chemistry, Combined with Optical Fibre, Offers a Novel Approach to Measuring Dissolved Oxygen and pH Levels with Many Promising new Applications

Advances in high-performance sensor materials and optoelectronics have enabled novel optical sensors for use in a diverse array of markets including the life sciences, environmental, food and beverage, process control, and aviation. Compared to traditional electrochemical sensing techniques such as galvanic, paramagnetic, and fuel cell sensors, these optical sensors (sometimes called "optrodes," as in optical electrodes) can be made in small, customizable form factors. They also have faster response, provide long-term calibration-free stability, are chemically inert, and couple easily to optical fibres for remote measurements. The principle of operation for optrodes is to trap a target-sensitive fluorophore or pH indicator dye in a host matrix that can then be applied to the tip of a fibre, flat substrate, adhesive membrane, or other surface. Optical fibres are particularly versatile because they can be made into probes of many sizes and shapes and can be jacketed for deployment in harsh environments. The sensing portion of the fibre probe is the tip, which can be made in sizes from 50 to more than 1000 µm in diameter.

Oxygen sensor

Oxygen optrodes are relatively new compared to electrochemical sensors. As chemistries and detector electronics improve, the use of optrode sensors is increasing, especially in the environmental, life-sciences and food-packaging markets. Most optrodes use a polymer-based host matrix to trap the fluorophore. Polymer-based oxygen (O_2) optrodes have the advantage of being able to be produced in volume with excellent lot-to-lot repeatability for calibration consistency. The main disadvantage is that polymers themselves fluoresce and promote photodegradation of the fluorophore, so the overall operating lifetime is limited.

Another chemistry first pioneered as a host matrix for O_2 sensing in the 1990s uses sol gels (see *Fig. 1*).[1, 2] Sol gels are a nanoporous, glass-like material that typically consist of metal alkoxide molecules that have been mixed with water and solvent to create a homogeneous partially polymerised liquid called a sol. The fluorophore is dissolved in the sol that is then applied to the substrate host (fibre tip or flat substrate) as a thin film, dried and cured to a hardened glass-like substance. Sol gels are widely used in many manufactured products as protective coatings, and are also easy to manufacture in high volume.

Sol gels offer some unique advantages compared to polymer technology. These include superior bonding to a wide range of substrates - they do not chemically bond to the sensor indicator, but instead "cage" or physically encapsulate the molecule, which provides better stability of the indicator molecule and makes the sol gel more versatile in terms of the range of indicators that can be trapped. The sol gel polarity and porosity can be tailored by changes in recipe and curing details to match the requirements of the target sample chemistry. So, for example, pH sol gels are made hydrophilic, O_2 sol gels are made hydrophobic, and sol gels for use in hydrocarbons like jet fuels are made both hydrophobic and oliophobic (repels long chain hydrocarbons).

In addition, sol gels exhibit superior optical properties—they can be made transparent, and readily transmit light from the ultraviolet through the near-infrared. Available sol-gel probe chemistries include standard materials that are used for gases and aqueous samples. These chemistries are used widely for environmental monitoring, and other relatively benign gas and liquid samples. An oliophobic, hydrocarbon-resistant formulation is used for compatibility with oils, alcohols, and hydrocarbon-based liquids and vapours. This has been tested successfully in aviation fuels, gasoline, diesel fuel, hydraulic fluids, and wines. The sol gels can be used with a ruthenium-based fluorophore for the 0% to 100% oxygen range. A platinum-poryphrin fluorophore is used for trace amounts of O_2 in the 0% to 5% range. Sensitivity of this sensor is in the low parts per million of O_2 in gas, and low parts per billion in liquids.

How does the sensor work

The fibre optic and sensor tip are illuminated with a blue LED creating a red luminescence. Luminescence generated at the tip is collected by the probe and carried by the optical fibre to a phase fluorometer. When O_2 in the gas or liquid sample diffuses into the thin-film coating, it dynamically quenches the fluorescence.

The degree of quenching correlates to the collision frequency between O_2 molecules and the excited state of the fluorophore, and is therefore directly reactive to the partial pressure of O_2. The quenching is observed as a decrease in the average fluorescence lifetime, which is detected as a phase shift between the fluorescent signal and a pulsed blue LED.

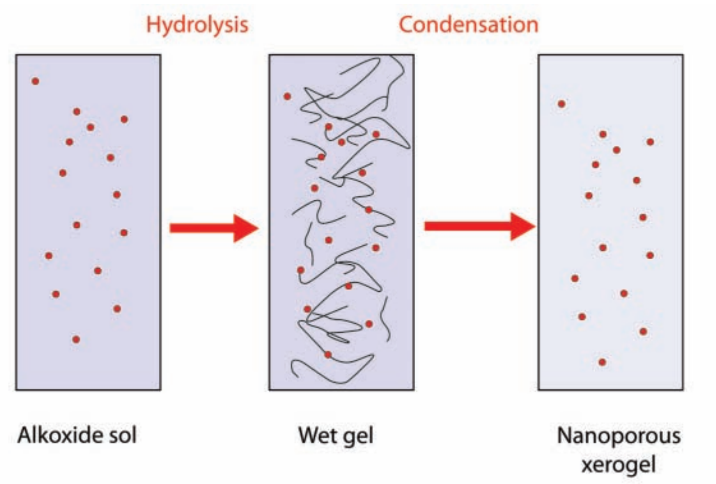

Figure 1. The sol-gel process involves the transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymeration reactions to form a colloidal suspension, or a "sol." Further processing of the "sol" enables ceramic materials in different forms to be made.

The change in phase (or lifetime or intensity) and pO_2 are related by the Stern-Volmer equation. Probes are calibrated by exposure to known levels of pO_2 and fitted with linear Stern-Volmer plots or polynomials for extended ranges. Temperature and total pressure compensation calibrations are determined in a similar fashion.

Advantages of the oxygen optrode

Fibre optic oxygen probes have several advantages over electrodes in environmental monitoring applications. Sol gel coating based sensors are not susceptible to biofouling as severely as polymer-based sensors; oxygen optrodes do not consume oxygen and therefore there is no need to stir the sample. Sol gel coating lends itself to adverse environments where there are harsh chemicals and minimum maintenance is desired.

Revolutionary pH technology

Advances in the sol-gel chemistry have led to the development of a unique hydrophilic fibre-optic pH sensor offering the same fibre and probe capabilities as the oxygen optrode.[3] The sensor is based on measuring the ratio of absorbance of a pH indicator dye at two wavelengths. The ratiometric method is immune to changes in intensity and moderate changes in dye concentration due to leaching, plus it is easy to calibrate.

Figure 2. Oxygen probes have an outer stainless-steel sheath.

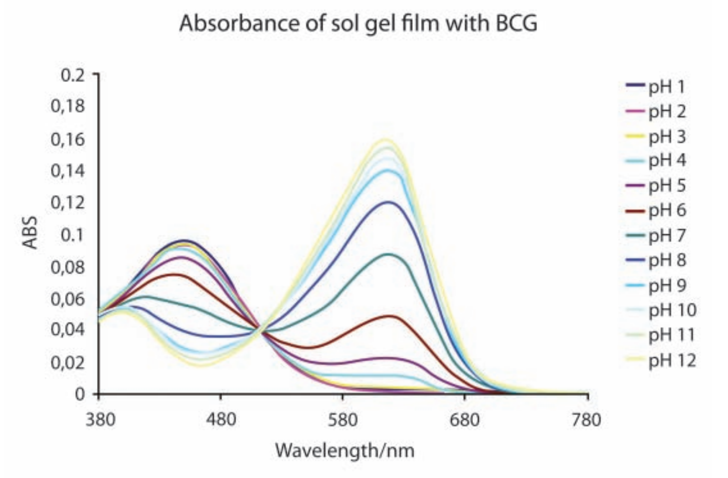

Figure 3 - Plotting absorbance versus wavelength at several levels of pH for a BCG optrode shows that the alkaline form of the indicator absorbs at about 620 nm and the acidic form absorbs at about 450 nm. At about 550 nm both forms have the same molar absorptivity—this is the isobestic wavelength.

Calibration consists of exposing the optrode to standard buffer solutions. Different pH indicators may be trapped in the sol gel for use in different pH ranges. The precision of the sensor is limited by the precision of the spectrophotometer and the total absorbance of the sensor. For an indicator with an absorbance of 1, and a spectrophotometer with a precision of 0.001 AU, a pH precision of ~0.001 pH units is possible.

The bromocresol green (BCG) optrode is responsive from pH 5 to 9, ideal for environmental and biological systems, and many industrial processes (see *Fig. 3*).

Visual-based colorimetric pH devices were made for the aquarium industry in the late 1980s. Ocean Optics pioneered the transfer of this technology for use as optrodes in the early 1990s. The material was based on polymer films that trapped the indicator molecules. These sensors were slow and the indicator gradually leached out, which limited their usefulness. The new sol-gel formulation is a major advance that offers a fast response rate of less than five seconds, very stable calibration (good for over a month with only a single baseline correction), and can easily be incorporated into a variety of product packages.

In addition, the sol gel can be applied to probes or as a coating to cuvettes, Petri dishes, microtiter plates, flow cells, or other media where the sample volume may be limited. Unlike other optical pH systems that measure fluorescence, this system is ratiometric and immune to drift; the sensors can be stabilized by steam or gamma radiation and they can be used with O_2 optrodes to provide pH and O_2 sensing in a small common package. Furthermore, these optrodes can use "off-the-shelf detection"- miniature fibre-optic spectrometers, or existing spectrophotometers.

Applications include bioreactor monitoring (see Laser Focus World, March 2008, p. 65; www.laserfocusworld.com/articles/SELKER), cell culture monitoring, waste water discharge monitoring, atmospheric/acid rain measurement, medical device application for blood and body fluid measurements, and field portable applications to name a few.

References

1. W. Wang, C.E. Reimers, M.R. Shahriari and S.C. Wainright, The Marine Technology Society Annual Conference Proceedings 1 (1998).

2. M. Krihak, M. Murtagh and M.R. Shahriari, Chemical, Biochemical and Environmental Fiber Sensors VIII, Proc. SPIE 2836 (1996).

3 "Upendra H. Manyam (Ph.D. thesis), M.R. Shahriari (thesis advisor) and George Sigel (thesis co-advisor), Application of Dye-Doped Sol gel for pH Sensing, Ph.D. thesis, Rutgers University, NJ (March 2006)

AUTHOR DETAILS

Bob Kearton
Manager System Sales

Mahmoud Shahriari
Chief Scientist of Sensors Business unit

Jason M. Eichenholz
VP Research and Development

Ocean Optics
4301 Metric Drive,
Winter Park,
FL 32792.
Web:
www.oceanoptics.com