

# Detecting Hydrogen with Chemochromic Thin Films

Hydrogen is generating considerable attention as a medium to store and transport energy and as a fuel for transportation (see *The Industrial Physicist*, February/March 2002, pp. 22–25). On January 9, U.S. Secretary of Energy Spencer Abraham announced a new public–private partnership to promote the development of hydrogen as a primary fuel for cars and trucks.

Freedom CAR (CAR stands for Cooperative Automotive Research) replaces the Partnership for a New Generation of Vehicles, which pushed the development of hybrid gasoline–electric vehicles. The new program focuses on the development of technologies for hydrogen-powered fuel cells. Analytical studies (well-to-wheels comparisons of fuel pathways and greenhouse-gas emissions) show that large reductions in petroleum use and greenhouse-gas emissions can be achieved by using fuel cells to power vehicles.

Hydrogen is a “clean” fuel, in that its use in fuel cells produces only heat and water (see *The Industrial Physicist*, August/September 2001, pp. 14–17). Although nearly all hydrogen is currently made from natural gas, using it in a fuel-cell vehicle reduces primary energy use and net greenhouse-gas emission by about 50% when compared to current internal-combustion engines. Future hydrogen production using nuclear power and renewable technologies (photovoltaics, wind, photocatalytic hydrolysis, biohydrogen, biomass, and solar-thermal reforming) will reduce greenhouse-gas emission to very low levels.

A public concern exists about the safety of using hydrogen. It is a flammable gas that burns in mixtures from 4% to 74% in air. The public’s perception of hydrogen’s danger dates back to the Hindenburg disaster of May 7, 1937. It is debatable whether hydro-

gen caused that disaster—the conclusion at the time. The hydrogen combustion may have resulted from a fire that ignited elsewhere on the airship. Nevertheless, because hydrogen is a flammable gas, it must be generated, stored, and used with care.

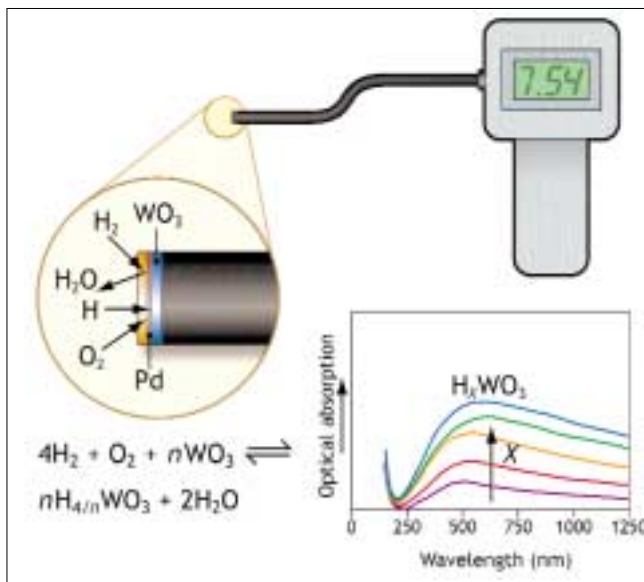
Handling hydrogen requires safety pre-

atoms, such as hydrogen—deposited on the end of a polymer or glass fiber-optic cable (see figure). In the presence of hydrogen, the chemochromic films undergo changes in the way they interact with light. A probe beam propagating down the fiber detects the change in optical properties of the film stack, either in transmissive or reflective modes. This detection of hydrogen requires no power input other than the probe beam of light. Thus, the sensor tip is inherently safe because there is no ignition source, such as a wire, associated with it.

The chemochromic materials that we use are derived from electrochromic materials described in the seminal work of Satyen Deb during the mid-1960s and early 1970s at American Cyanamid Company. Deb is currently NREL’s director for basic sciences. These materials are transition metal oxides, which undergo dramatic changes in absorption in the visible spectrum with the insertion of electrons and intercalating ions, typically lithium or hydrogen. The charges are inserted or removed reversibly by the application of small electric fields; hence the name electrochromic.

Much of this early work was oriented toward making display materials, but recently, interest has focused on using these oxide materials in the windows of buildings to control the transmission of light. In 1984, Japanese scientists Kentaro Ito and K. Kubo suggested that these metal oxide materials might be useful for detecting hydrogen gas if a suitable catalyst to dissociate the hydrogen molecule covered them. Platinum group metals perform this function and diffuse hydrogen readily, which forms the basis of our fiber-optic sensor.

The end of the cable is coated with approximately 500 nm of a chemochromic material—tungsten oxide ( $\text{WO}_3$ ) is a good prototype—which is overlaid with a hydrogen-dissociation catalyst (palladium and its alloys work best). When hydrogen is present in the air, some of it dissociates on the catalyst sur-



Hydrogen tends to dissociate on this palladium-covered chemochromic tip of tungsten oxide, causing a change in color that is sensed by the light beam in the fiber and read out by the control package.

cautions, and we can expect enactment of stringent safety codes before the public accepts it as a transportation fuel or a replacement for natural gas. Scientists are confident that hydrogen will meet its potential because these safety issues are now being addressed. Part of the solution will be safe, reliable, sensitive, fast, lightweight, inexpensive hydrogen sensors to provide an early warning or initiate action in the event of a leak and accumulation of the gas.

At the National Renewable Energy Laboratory (NREL) in Golden, Colorado, a team of physicists and chemists is working on a technology to meet the requirements of the sensors. Our design consists of chemochromic thin films—in which optical properties change upon the insertion of light


face and then diffuses through the catalyst layer and into the chemochromic layer to cause a change in color. Recently, we developed new chemochromic materials, including porous  $\text{WO}_3$ , vanadium oxide ( $\text{V}_2\text{O}_5$ ), and a tungsten-doped nickel oxide, which show increased sensitivity, speed, and stability. The sensitivity of these materials is 200 to 1,000 ppm of hydrogen in air, depending on the material selected, and the response time (0–90% of signal) is less than 1 s. When  $\text{V}_2\text{O}_5$  is used, the thin-film system is extraordinarily stable to cycling in higher concentrations of hydrogen, even up to 100%.

So far, this is a compelling story of sensors working smoothly in the laboratory. However, when the sensor materials are stored or used under less than ideal conditions, such as in the presence of pollutants in the air, the sensitivity and speed of the devices change with time. After studying these changes by using surface, Fourier-transform infrared, Raman, and electrochemical-impedance spectroscopies, we

believe that we understand how these changes evolve. We are developing methods to stabilize the probe tip in ordinary atmospheres and render pollutants harmless. Our methods have worked well, and we have tested sensors that have functioned without degradation for more than a year under ambient conditions.

Other questions have been raised about the sensors. For example, how do they behave when cycled in hydrogen at various temperatures and relative humidities? Sensors show a significant increase in response time at relative humidities greater than 50%, and they have a pronounced peak in sensitivity at room temperature. Below the freezing point, the accumulation of ice slows response time. We are looking at ways to passively mitigate the loss of performance caused by temperature and humidity changes. Heating is one answer, but we want to avoid running a wire to the sensor tip.

Not all of the issues have been solved regarding the use of chemochromic materi-

als on a fiber-optic cable to sense the presence of hydrogen. However, we are well on the way to meeting all of the criteria needed to provide reliable safety sensors at low cost. If we achieve that goal, we will remove one impediment to the development of a hydrogen-based economy, particularly regarding its use as a transportation fuel. 

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