New hydrogen sensor faster, more sensitive

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The same kind of chemical coating used to shed rainwater from aircraft and automobile windows also dramatically enhances the sensitivity and reaction time of hydrogen sensors. Hydrogen sensor technology is a critical component for safety and other practical concerns in the proposed hydrogen economy. For example, hydrogen sensors will detect leaks from hydrogen-powered cars and fueling stations long before the gas becomes an explosive hazard.

The discovery was made by a team led by Zhili Xiao, a physicist in the Materials Science Division at the U.S. Department of Energy's Argonne National Laboratory and an associate professor of physics at Northern Illinois University. The scientists demonstrated that the enhanced sensor design shows a rapid and reversible response to hydrogen gas that is repeatable over hundreds of cycles. A report on the team's research was published in May in Applied Physics Letters.

The sensor material is made by depositing a discontinuous palladium thin film on a glass slide coated with a grease-like self-assembled monolayer of siloxane anchored to the surface.

“By adding the siloxane self-assembled monolayer, we have changed the thin film dynamics,” said Michael Zach, a chemist and holder of the Glenn Seaborg Postdoctoral Fellowship at Argonne. “Other sensors have a response time of several seconds upon exposure to 2 percent hydrogen; ours works in tens of milliseconds.” Also, the scientists reported that the enhanced sensors are sensitive enough to detect hydrogen levels as low as 25 parts per million (ppm), far below hydrogen's lower explosive limit around 40,000 ppm. Their sensitivity and speed are superior to any available commercial sensors.

Palladium is an ideal material for hydrogen sensing because it selectively absorbs hydrogen gas and forms a chemical species known as a palladium hydride. Thick-film hydrogen sensor designs rely on the fact that palladium metal hydride's electrical resistance is greater than the metal's resistance. In such systems, the absorption of hydrogen is accompanied by a measurable increase in electrical resistance.

However, a palladium thin-film sensor is based on an opposing property that depends on the nanoscale structures within the thin film. In the thin film, nanosized palladium particles swell when the hydride is formed, and in the process of expanding, some of them form new electrical connections with their neighbors. The increased number of conducting pathways results in an overall net decrease in resistance.

Palladium is good at “wetting” bare glass surfaces – it spreads across the glass in puddle-like clusters a few nanometers thick and tens of nanometers across. After pre-coating the glass with the siloxane monolayer, the Argonne scientists saw a remarkable shift in the size and spatial distribution of the palladium. Like water beading on the surface of a freshly waxed car, the palladium formed granular clusters just a few nanometers across. The gaps between neighboring palladium clusters on the siloxane-coated glass were more numerous and ten times smaller on average than the gaps between the much larger, spread-out clusters on the bare glass.

“The shorter gap distance is important for giving you a fast, sensitive response,” said Tao Xu, a chemist and the first inventor of the submitted patent application on fast hydrogen sensors. Even a slight swelling of the clusters produces many more new electrical contacts between neighbors and links together many new pathways for an electrical current to travel.

The scientists also have evidence that the surface treatment of the glass reduces the adhesion – or “stiction” – between the metal and glass that hinders the expansion and contraction of the palladium nanoparticles on bare glass. This effect contributes to the increased speed of the sensor response.

The scientists spent nearly a year optimizing the procedure to make the palladium films on coated glass, and they developed a new test system that could inject hydrogen quickly enough to test the sensors on a millisecond time scale. They say their approach to making sensors is easily scalable to an industrial level. “We are using techniques that the semiconductor industry already uses,” Zach said.

The sensor will be affordable too. Although palladium is an expensive precious metal, Zach estimated that the amount in each sensor is so small that the metal cost is less than a penny.

Several outstanding questions include whether the sensors can be made to withstand poisonous contaminants in the air and whether the sensors will stand up to long-term operation. Wai-Kwong Kwok, leader of the Superconductivity and Magnetism group in the Materials Science Division, expressed confidence that these issues can be handled on an engineering level. The sensors are being developed for commercial use by an industrial partner in collaboration with Argonne.

Source: Argonne National Laboratory