Metal hydride based optical hydrogen sensors

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The transition towards a sustainable energy system poses an increasing demand for hydrogen as an energy carrier. However, unfortunately the use of hydrogen comes with a safety issue: mixtures of hydrogen with air can be flammable or even explosive under certain conditions. As such, hydrogen sensors that can detect the tiniest leakage of hydrogen or, for example, asses its purity are essential for its large scale implementation. Although hydrogen sensors are available that do the trick for some applications, they feature quite some serious shortcomings: they are relatively large, expensive, and feature a small operating range in terms of hydrogen partial pressure/concentration. Most of all, they typically require the presence of oxygen and often rely on electric sparks, posing a serious safety hazard in the neighbourhood of (leaking) hydrogen. Metal hydride based optical hydrogen sensors do not have these shortcomings and can be made small, cheap and inherently safe.

Metal hydrides are formed when metals absorb hydrogen. This special property of metals was already known since the nineteenth century when Thomas Graham discovered that palladium can accommodate 'eight to nine hundred times its volume in hydrogen gas'. As such, metal hydrides have been considered to store hydrogen as the volume density is much higher than for instance liquid or highly pressurized gaseous hydrogen. However, although the volumetric density is relatively high, the gravimetric density is, even for lightweight metal hydrides as MgH_2, modest. Apart from this, a major drawback is that while absorption is relatively fast, desorption can be slow and the strong negative enthalpy of formation of the metal hydride implies that a large amount of heat needs to be supplied when hydrogen is desorbed. While decades of research have aimed to improve this by alloying or nanosizing the materials (e.g. making small nanospheres of it), this technology has not been applied on a large scale.

The propensity of metal hydrides to adsorb hydrogen can also be used to create hydrogen sensors. The principle behind these sensors is simple: as illustrated in Figure 1, a change of the hydrogen concentration in the environment of the sensor emanates in a change of the hydrogenation of the metal hydride (i.e. x in MHx changes, with M being a metal). In turn, this alters the dielectric function and thus the optical properties of the metal hydride sensing layer. One of the many possibilities to create a device out of this is to deposit a metal hydride sensing material on the tip of an optical fibre (Figure 2). Light that is guided through an optical fibre is then reflected by the sensing layer deposited at the top of the fibre. The intensity of the reflected light is monitored by a photodetector and can thus be directly related to the hydrogen concentration in the environment of the sensing layer.
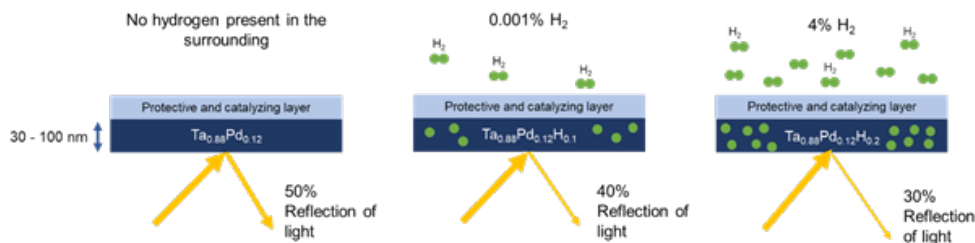
Figure 1. Schematic illustration of the working principle of optical hydrogen sensors. In the proximity of hydrogen, a metal hydride (in this case an alloy of tantalum (Ta) and palladium (Pd)) absorbs hydrogen). The higher the partial hydrogen pressure/ hydrogen concentration in the area, the more hydrogen the material absorbs. When the material absorbs hydrogen, its optical properties change. By for example measuring the amount of light reflected by the material one can determine the hydrogen pressure or concentration.

The trick in constructing an optical hydrogen sensor is in finding a suitable sensing material with a thickness of a few tenths of nanometres. To find out what is a good sensing material, it is instructive to consider Beer-Lambert's law that describes the optical transmission T of a thin film of material with thickness d:

$$T(x, d, \lambda) = \frac{I(d)}{I(d = 0)} = \exp[-\alpha(x,\lambda)d(x)],$$

where $\alpha(x,\lambda)$ is the linear attenuation coefficient of the thin film, λ the wavelength of the light and x the hydrogenation of the sensing layer (x in MHx) that depends on the partial hydrogen pressure P_{H2}, which is the number of hydrogen atoms per unit volume in the environment of the sensor.

For an accurate hydrogen sensor, we want large changes of the signal/optical response with a change in the hydrogen pressure of the sensor. Thus, we want a material where (i) a different partial hydrogen pressure results in a large change of the hydrogenation of the layer (dx/dPH2 should be large), (ii) the change in optical properties of the material is large when the hydrogenation changes ($|d\alpha(x,\lambda)/dx|$ should be big), and (iii) the hydrogenation of the layer does not depend on the history of the sensor. Furthermore, we want a sensor that can detect a wide range of hydrogen concentrations/pressures, so x should change monotonously with PH_2 over a large pressure range. Apart from that, the sensor needs to be stable, not sensitive to poisoning by other chemical species (CO, NO_x etc.) and have a fast response.
In order to understand what materials satisfy the-

se requirements, let's first dive a bit deeper into the physics of metal hydrides. The amount of hydrogen absorbed by a metal depends on the partial hydrogen pressure and the temperature. At a given temperature, it can be described by the Pressure–Concentration–Isotherm (PCI). To illustrate this, let's consider the phase diagram of palladium, shown in Figure 3. For relatively small x, a so-called α-phase exists in which x increases as the hydrogen pressure increases. As the pressure further increases, hydrogen continues to be absorbed until elastic H−H interactions become dominant and a β-hydride phase starts to nucleate. Subsequently, the β-phase grows at a constant pressure at the expense of the α-phase (see the plateau in the PCI diagram). When the α-phase is entirely converted into the β-phase, a higher hydrogen pressure results in a continuous increase of the hydrogen content of the β-phase.

One property of a first-order phase transition is that it involves hysteresis. In this particular case, it implies that the pressure at which the phase transition occurs when the pressure is increased deviates from when it is decreased. As such, the hydrogenation of the layer depends on the pressure history, and thus, the response of the hydrogen sensor, which is highly undesirable.

Palladium is one of the most widely considered materials for hydrogen sensors. It has a reasonable sensing range at room temperature with good optical contrast (dx/dP$_{H2}$ and $|d\alpha(x,\lambda)/dx|$ are both large) and can readily dissociate molecular hydrogen (H2)
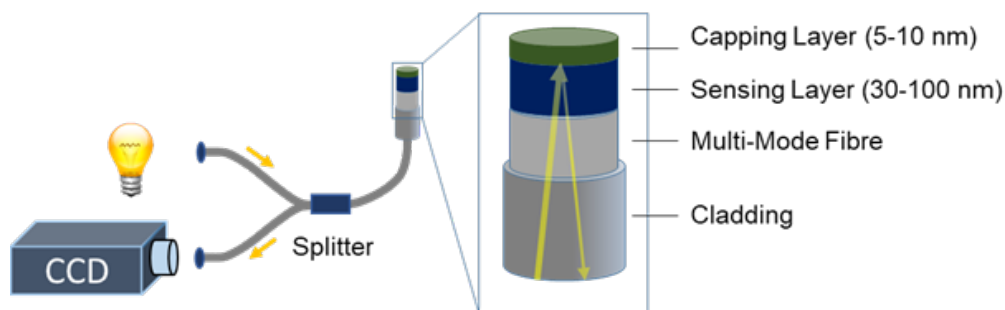

Figure 2. Schematic illustration of a micro-mirror optical hydrogen sensor. Light is coupled into a fibre in which it is transported to the tip of the optical fibre sensor. This tip partially reflects the light, and the reflected light is then passed back through the fibre and the splitter. The reflected light is subsequently measured by a photodetector as, for example, a charge-coupled device (CCD). When the hydrogen pressure changes, the hydrogenation of the sensing layer (30−100 nm) changes, resulting in a change of the optical properties and thus the amount of light reflected by the layer stack and detected by a photodetector. A capping layer is used to prevent oxidation of the sensing layer and to catalyse the hydrogen adsorption.
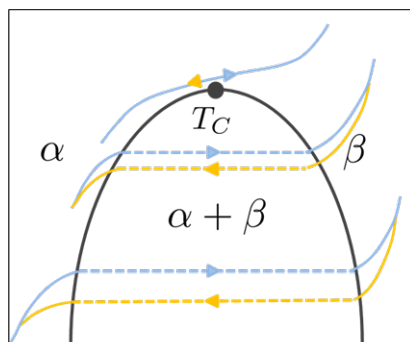
Figure 3. Typical temperature T and hydrogen-to-metal ratio (x in MHx) phase diagram of a typical metal hydride and examples of pressure-composition-isotherms (PCIs).

into atomic hydrogen as required for a fast response. However, for bulk palladium, a first-order phase transition always occurs below its critical temperature $T_c \approx 270\ °C$, making it thus unsuitable for most applications as it will have a hysteretic response.

To develop a hydrogen sensor where the reading does not depend on the pressure history, we thus need to find a material with a lower critical temperature. One way of achieving this is to alloy palladium. For example, by alloying palladium with 20% of gold, we can reduce TC below room temperature. As such we thus successfully suppressed the undesirable first-order phase transition. However, this comes at the expense of a much lower sensitivity as dx/dP_{H2} is much lower.

Another approach is to consider other metals than palladium. One metal that we recently considered is tantalum that has a critical temperature of $T_c \approx 61\ °C$ reported for bulk (powder) material. As such it would still seem unsuitable for room temperature hydrogen sensing. Luckily, this turns out not to be the case. Remember that the layer of material we deposit is only a few tenths of nanometres thick and deposited on a fibre or substrate. The response of such a thin film to hydrogen may deviate substantially from that in bulk because surface effects may play a role and/or due to confinement effects. To understand what confinement implies, one has to realize that when metals absorb hydrogen, they typically expand to accommodate the hydrogen in the lattice. In bulk, where all kinds of micro-meter size grains are present, this expansion can occur in all directions. In our thin films, this is not the case, and expansion

can only be realized in one direction. This induces locally large stresses, which significantly affect the thermodynamics and thus the critical temperature of the system. By exploiting these effects, we can thus also design a hydrogen sensing material with a lower critical temperature. Besides studying the response of our materials with optical measurement, we make extensive use of both X-ray and neutron radiation to understand what is actually happening in the material at the atomic level when it is exposed to hydrogen.

One material we recently developed is tantalum-palladium. Here, we optimally make use of both alloying and nanoconfinement effects. In combination with a catalytic layer to dissociate the molecular hydrogen (and thus ensure a fast response), tantalum-palladium has remarkable properties including hydrogenation that changes monotonously with the hydrogen pressure over seven orders of magnitude. As such, we can achieve a hysteresis-free sensing range of over seven orders of magnitude in pressure with an almost constant sensitivity. If you would translate this to a scale that is well known, it would correspond to a kitchen scale that can measure anything from a few grams of flour to the weight of an elephant, and all with the same relative accuracy. These special properties have not remained unnoticed, and we have now applied for a patent for this discovery and are interacting with companies that are interested in developing it into a commercially available product. Yet, our search for hydrogen materials has not halted, as we still want to stretch the limits. For example, we want to find materials that can be used at low temperatures, posing a whole series of new challenges. ⚛
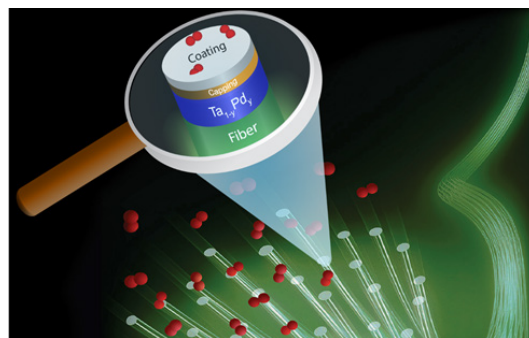

Figure 1 Artist impression of a metal hydride optical hydrogen sensor