Optical sensor for online-monitoring of oxygen traces in hydrogen electrolysis

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ARTICLE INFO

ABSTRACT

Hydrogen is an important source material in the chemical industry and plays an important role in peripheral and regenerative energy supply like e.g. fuel cells. In particular for hydrogen electrolysis the oxygen concentration is a crucial parameter in respect of the quality of the produced hydrogen and safety aspects. Here we present a spectroscopic sensor, which is appropriate for online-monitoring of oxygen at high pressures. It shows no cross-sensitivities to water and hydrogen, and its optical power is well below the limit of explosion.

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1. Introduction

Up to now, hydrogen, mostly produced with thermal reformers, has to be transported over long distances. Often the condensation and compression are more extensive than the production itself. Hydrogen electrolysis offers the advantage of local supply with uninterrupted service, low cost and a high purity. In contrast to thermal reformers, there is no CO_2 emission during the process and no fossil fuels are needed as base material. In addition, hydrogen electrolysis is well suited for the storage of renewable energy [1,2], since electrolysis as well as fuel cells provide a very high efficiency [3,4].

A typical hydrogen electrolysis set-up is depicted in Fig. 1. An electrical power source is connected between two electrodes, which are placed in water. Due to the electric current being passed through the water, the water decomposes, so that oxygen appears at the cathode and hydrogen at the anode. A membrane between the two electrodes is used to separate the hydrogen from the oxygen. Anyway, traces of oxygen can diffuse through the membrane. To guarantee the purity of the produced hydrogen and to detect leaks in the membrane, the oxygen concentration has to be monitored continuously. In particular it has to be assured that the oxygen concentration is well below the explosion limit of 4%. For this application a gas sensor requires a low detection limit, no cross-sensitivities in particular for water, the possibility for online-monitoring and a low energy transfer into the gas to prevent the risk of explosion. These demand advise spectroscopic sensors for oxygen detection in hydrogen electrolysis. However at the typical operation pressure of hydrogen electrolysis systems (up to 30 bar),

usually the effect of pressure broadening of absorption lines and the effect of line-mixing strongly complicate spectroscopic trace gas measurements.

2. Set-up of the optical sensor

The spectroscopic oxygen sensor is depicted in Fig. 2. The light source is a vertical cavity surface emitting laser (VCSEL) operating at 763 nm wavelength. The optical power of 0.5 mW/mm² emitted by the laser is well below the risk of explosion of 5 mW/mm². Here the very weak electric dipole forbidden transition of the oxygen a-band ranging from 759 nm to 769 nm is used for absorption measurements [5,6]. Scanning the wavelength of the laser over the absorption line is achieved by variation of the injection current. A beam splitter is used to divide the beam into two beams. The first one passes the absorption cell two times and is detected by a photodiode, so that an absorption path length of $L = 1$ m is achieved. The second one is directly detected by a photodiode to profit from the technique of the "balanced receiver" [6] which is used to reduce the intensity noise of the laser. The absorption cell is pressure resistant up to 30 bar and is sealed by wedged BK7 windows to avoid interference fringes. Using Beer–Lamberts law, the oxygen density n can be determined with the knowledge of the intensity with and without absorption:

$$\frac{I}{I_0} = \exp(-\alpha_{(\nu)} nL). \tag{1}$$

Here I/I_0 is the laser intensity with and without absorption, α is the absorption coefficient, n the density of the absorbing molecules and L the absorption path length. With the ideal gas equation and the knowledge of the total pressure the oxygen concentration can be easily calculated.

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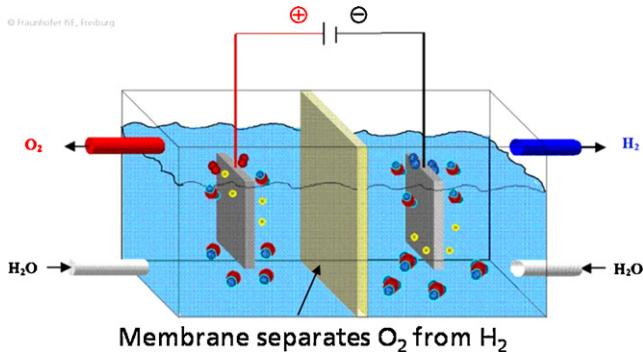E-mail address: benjamin.scherer@ipm.fraunhofer.de (B. Scherer).

Fig. 1. Schematic set-up of an hydrogen electrolysis system. Leakages in the membrane can increase the risk of explosion.

3. Theory of pressure broadening of the oxygen a-band

Pressure broadening of absorption lines is caused by elastic or inelastic collisions and is therefore also called "collision-broadening". If both collision partners are from the same sort of molecule, this process is denoted as "self-broadening", otherwise as "foreign-broadening". The self-broadening coefficient as well as a large number of foreign-broadening coefficients for absorption lines of the oxygen a-band are well known in the literature [7–10], but, to our best knowledge, up to now there is no experimental data available, which describes the pressure broadening of oxygen in hydrogen.

In principle, pressure broadening limits gas measurements with tunable laser absorption spectroscopy to low pressures, at which the absorption lines are still separated. At higher pressures the absorption lines completely overlap and a large wavelength tuning range of the laser is required to obtain information about the gas concentration from the spectroscopic data. As an example in Fig. 3 the p-branch of the oxygen a-band at 1 atm and 10 atm measured in pure oxygen (self-broadening) with an widely tunable polarization stabilized VCSEL is shown [5]. Here, at 10 atm the absorption lines completely overlap so that a widely tunable, mostly very expensive laser source has to be used to achieve reliable concentration measurements.

Pressure broadening of the oxygen a-band is mainly caused by elastic collisions. Therefore there is per definition no kinetic energy transfer between the collision partners. Intermolecular interactions of the collision partners cause a shift in wavelength of the absorption lines which is different for different energy levels, different molecules and different electronic configurations of the collision partners. It is positive for repulsive potentials and negative for attractive potentials and depends strongly on the distance R_{AB} between the centers of mass of collision partner A and B. As the average intermolecular distance $\bar{R}_{AB}$ and also the distribution around $\bar{R}_{AB}$ depends on pressure, there is a shift in absorption frequency $\Delta v_{s,i}$ and also a broadening of the absorption lines $\Delta v_{c,i}$ with increasing pressure. Neglecting other broadening mechanism like e.g. Doppler-broadening the resulting absorption line shape is described by a Lorentz profile:

$$\phi_i = \frac{1}{\pi} \frac{\Delta v_{c,i}}{(v - v_{0,i} + \Delta v_{s,i})^2 + (\Delta v_{c,i}/2)^2}, \qquad (2)$$

whereas $\Delta v_{s,i}$ is the pressure shift and $\Delta v_{c,i}$ the pressure broadening of the absorption line i. The pressure broadening of absorption line i is usually described by the pressure broadening coefficient $\gamma_{j,i}$ [5,10]:

$$\Delta v_{c,i} = P \sum_j X_j \gamma_{j,i}. \qquad (3)$$

Here P is the total pressure P and X_j the mole fraction of the jth component of the gas mixture. The total broadening is therefore the sum over self- and foreign-broadening effects caused by different sorts of molecules j contained in the gas mixture.

Another definition for pressure broadening is the broadening cross-section, which is related to the broadening coefficient as follows [10]:

$$\sigma_{j,i} = \frac{\gamma_{j,i} k_B T}{\langle v \rangle}. \qquad (4)$$

Here T is the temperature, k_B the Boltzmann constant and $\langle v \rangle$ the average velocity of the molecules in the gas mixture.

From the elastic scattering theory from Weisskopf and Wigner [10] it is known that the broadening cross-section is mainly dependent on the polarizability α, the reduced mass μ of the collision pair and the order n of the intermolecular interaction potential [10]:

$$\sigma_{j,i} = C \alpha^{(2/n-1)} \mu^{(1/n-1)}, \qquad (5)$$

where C is a constant, which is independent from the pertuber. Measuring the broadening cross-section of the oxygen a-band for different gas mixtures and applying a multidimensional fit on the data, the parameters C and n could be determined by the work of Pope [10]. The result is shown in Fig. 4. With the polarizability of hydrogen, $\alpha = 0.79$ Å^3 and the reduced mass of the O_2–H_2-collision pair, $\mu = 0.31 \times 10^{-26}$ kg from the theory of [10](Fig. 4) a foreign-broadening cross-section for hydrogen of $\mu \approx 0.7 \times 10^{-15}$ cm^2 is expected. This value is about twice as large than that of He and about half the value of the self-broadening cross-section.

4. Measurements

In Fig. 5 the absorption of the P9P9-line of the oxygen a-band measured during the electrolysis process at a pressure of 2 atm (top) and 10 atm (bottom) is shown. The measured absorption at 2 atm corresponds to an oxygen concentration of 0.71%, the absorption at 10 atm to an oxygen concentration of 0.18%. The noise equivalent concentration at 10 atm is 200 ppm (3σ) and
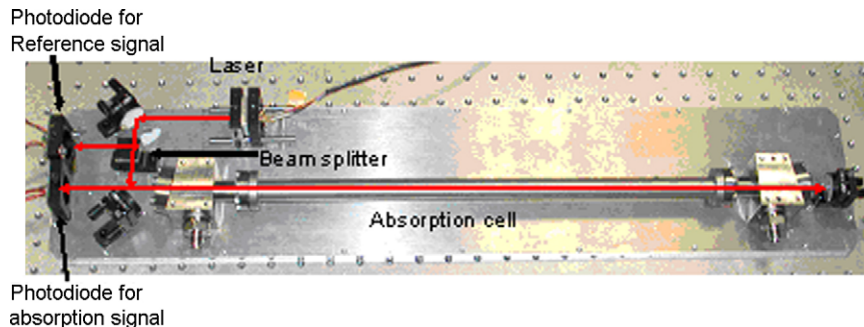

Fig. 2. Set-up of the optical oxygen sensor.