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Novel instrument and method for the investigation of small permeation fluxes of gases through different membranes

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ABSTRACT

In this study a new permeation measurement equipment is presented which is shown to be capable of measuring low and high gas fluxes through different membranes. The new membrane support system which is introduced here is suitable for thin membranes (>10 μm) and is expected to provide more accurate results than the design used in earlier permeation measurements.

In order to provide a glimpse of the possibilities of the new equipment, hydrogen permeation measurements through a low-density polyethylene (LDPE) and a nickel membrane are presented. The pressure difference dependence of the hydrogen fluxes measured agreed well with the behaviour expected according to Sieverts' law. In case of the LDPE membrane our results can be explained with the molecular diffusion of hydrogen, which agrees with literature data. As for the nickel membrane the results suggest that under our experimental conditions the speed determining step of the permeation is the atomic diffusion.

1. Introduction

The investigation of gas permeation through different membranes is of great interest. There are a lot of industrial processes based on the permeation properties of membranes. Hydrogen as permeating gas is particularly important as it is a prospective energy carrier and in the production of hydrogen membranes are widely used for purification [1–7].

As another interesting aspect of the investigation of permeation, the results also carry information about the elementary processes involved in the permeation. In case of a metal membrane and hydrogen as a permeating gas these processes include the adsorption and dissociation of the hydrogen molecules on the surface, the diffusion of hydrogen atoms through the metal and finally the recombination of these atoms and the desorption of molecules on the other side of the membrane e.g. [8]. Almost all of these processes are widely investigated. The properties of the surface and their effect on the processes taking place on the surface are of particular importance as these processes determine the usable life-time and hydrogen storage properties of metal hydride based hydrogen storage tanks e.g. [9–11] and they can strongly influence the permeation properties of metal membranes e.g. [12–14].

With the aid of the instrument presented in this work a wide range of experiments can be carried out, e.g. time-lag permeation measurements which can provide information about permeation coefficients, solubilities and diffusion coefficients in case of different metal and non-metal membrane materials. As the temperature of the membranes can be adjusted over a wide range the determination of the temperature dependence of these parameters is also possible.

Interpretation of the results of time-lag permeation measurements can be found in several articles e.g. [15,16]. The result of the evaluation of the diffusion equation is that in case of a membrane which has a given gas pressure introduced to one side and vacuum (zero gas

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partial pressure) on its other side the permeating flux (J ($mol_H\ s^{-1}\ m^{-2}$)) is proportional to the gas concentration solved in the near surface region of the high pressure side [15,16] of the membrane:

$$J = D\frac{c_S}{d} \tag{1}$$

where D ($m^2\ s^{-1}$) is the diffusion coefficient, d (m) is the thickness of the membrane and c_S ($mol_H\ m^{-3}$) is the solved concentration of the gas in the near surface layer of the membrane at the high pressure side.

The solved hydrogen concentration in equilibrium can be calculated with the aid of thermodynamic considerations. In case of polymer membranes the solved surface hydrogen concentration ($c_S^{H_2}$) is usually directly proportional to the hydrogen pressure p_{H2} (Pa) (k ($mol_H\ m^{-3}\ Pa^{-1}$) is a constant) since hydrogen dissociation does not take place on the surface [17]:

$$c_S^{H_2} = k \cdot p_{H_2} \tag{2}$$

In case of metal membranes and hydrogen the solved surface hydrogen concentration (c_S^H) in equilibrium is proportional to the square root of the hydrogen pressure (Sieverts' law) on the high pressure (p_{H2} (Pa)) side due to the dissociation of the hydrogen molecules on the surface of the metal [18], if the hydrogen pressure is not too high (k' ($mol_H\ m^{-3}\ Pa^{-1/2}$) is a constant):

$$c_S^H = k' \cdot \sqrt{p_{H_2}} \tag{3}$$

Hydrogen permeation in case of metals is a complex process and the pressure dependence of the permeating flux through a metal membrane can indicate which partial step is the rate limiting process in the permeation. If the rate limiting process with the applied experimental parameters is the diffusion, the pressure dependence of the permeating flux usually follows the Sieverts' law [8], given that the hydrogen pressure at the high pressure side is in the validity range of the Sieverts' law. In case of polymer membranes, hydrogen diffuses in molecular form, thus the rate limiting step cannot be determined easily, a linear relationship between the hydrogen pressure and the permeating flux is expected.

2. Materials and methods

Permeation experiments can be used in order to investigate the hydrogen–metal interaction in case of metals with very small reported hydrogen solubility (such as Al [19]). When experimenting with these metals extremely small hydrogen fluxes are expected, thus the most important requirement is the sensitivity of the measurement equipment. The final equipment shown here is not only capable of measuring small hydrogen fluxes through metal membranes, but it can also be used to investigate the permeation of other gasses (such as He) and high permeating fluxes with high sensitivity and to study the permeation properties of non-metal membranes as well.

2.1. New permeation measurement system

2.1.1. Schematics of the system

Fig. 1 shows the scheme of the new setup. The device consists of two chambers (high pressure and high vacuum chamber) separated by the membrane under investigation whose temperature can be measured and adjusted with the adjacent heating system between room temperature and 200 °C. The mounting system of the membranes is suitable for membranes of different thickness (it was tested from approx. 10–125 μm), also preventing them from damage even if there is overpressure on one side and vacuum on the other.

The high pressure side comprises a small, gastight chamber with known volume, a pressure sensor, a gas inlet/outlet valve system and an oil free fore-vacuum pump. The chamber can be evacuated to fore-vacuum and any arbitrary gas can be introduced to the chamber at the high pressure side with given pressure which can be measured with high accuracy as a function of time and stored on a computer.

The high vacuum part (the other side of the membrane) consists of a fore-vacuum pump, a turbomolecular pump and a vacuum chamber fitted with a cold trap cooled by liquid nitrogen (base pressure around 2×10^{-9} mbar). The pumps and the chamber can be separated from each other with a valve. The pressure in the chamber above the valve can be measured (MKS 909AR) as a function of time with high accuracy and recorded with a computer.

2.1.2. Membrane mounting

Similar measurement systems were used earlier by other research groups e.g. [4,20–22]. However the systems presented in the papers are tend to use thicker membranes with a simpler membrane mounting design and the permeation measurements were usually conducted at high temperature (above 200 °C). In case of low temperatures (under 200 °C) and materials with small solubilities and diffusion coefficients the thickness of the membrane becomes important, as the permeation flux is higher using thinner membranes (and the diffusion limited processes

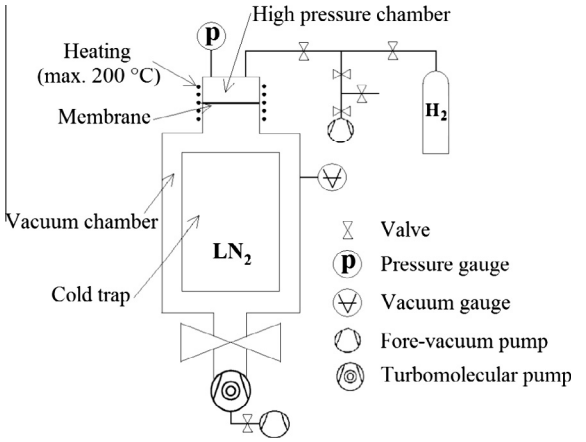

Fig. 1. The scheme of the high sensitivity permeation measurement setup for the investigation of permeation properties of membranes.