Current density effect on hydrogen permeation in PEM water electrolyzers

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ABSTRACT

Hydrogen permeation is an important phenomena for PEM water electrolyzers, due to several reasons as safety issues and efficiency loss. The present contribution deals with the measurement of hydrogen volume fraction within the anode product gas during PEM water electrolysis for different temperatures and cathode pressures. High cathode pressures lead to high anode hydrogen volume fractions close to the lower explosion limit of hydrogen in oxygen, which are caused by increased hydrogen permeation. It is shown that the results of the hydrogen volume fraction measurements can be easily converted into hydrogen permeation rates. Additionally, the experimental obtained permeation data indicate that hydrogen permeation increases linear with increasing current density. The impact of current density on the hydrogen permeation is very strong in comparison to the effects of temperature and pressure e.g. a current density increase of 1 A/cm^2 can causes a permeation increase comparable to a cathode pressure increase of 20 bar. In the second part of this contribution different theories to explain this strong dependence on current density are discussed. The most probable explanation is that due to mass transfer limitations a supersaturation of dissolved gas within the catalyst ionomer film arises that causes the investigated increase in permeation.

Introduction

Gas permeation through Polymer Electrolyte Membranes (PEM) has been widely investigated. In PEM water electrolysis it has high relevance with regard to safety issues, efficiency losses [1,2] and degradation [3]. Whereas the latter is an issue at high current densities, safety problems and Faradaic efficiency losses appear mainly at low current densities. However, thinner membranes and/or high pressures intensify all issues.

Permeation is influenced by a large number of different effects. Many of them have been analyzed. In particular the

research of Sakai and co-workers [4,5] is to be emphasized, who conducted one of the first comprehensive gas permeation investigations related to polymer electrolyte membranes. Sakai et al. [4] observed that the gas permeation rises with increasing temperature, water content, partial pressure and current density, but with decreasing equivalent weight and membrane thickness. Most of these effects have been frequently investigated afterwards e.g. Refs. [1,2,6–14].

An important parameter for the description of gas permeation through PEM-materials such as Nafion is the permeability coefficient that comprises of applying Fick's first law and Henry's law and is defined as the product of gas diffusivity and solubility of the membrane [15]. The main part of the gas

diffusivity and solubility of the membrane originates from the dissolved water within the membrane, whereas the part of the polymer is considerable smaller [5,6]. Both, the gas diffusivity and solubility of the membrane are mainly influenced by temperature [16]. In particular, the diffusivity has a strong temperature dependence, thus many research groups investigated this aspect e.g. Refs. [4,6–11].

The diffusivity and solubility for gas in liquid water are nearly pressure independent (within the regular operation range) [16], thus the permeability coefficient shows no pressure dependence as well [12]. Nevertheless, pressure has a powerful impact on gas permeation e.g. Refs. [4,7,9,11,12]. Barbir [11], for example, showed a linear increasing hydrogen permeation rate for gradients in hydrogen pressure up to 220 bar. This behavior can be described very well with a purely diffusive transport process. Furthermore, high pressure differences between anode and cathode can cause an additional convective permeation under certain conditions [7].

As previously mentioned the permeation process occurs especially in the membrane water. Thus, an increase in the membrane water content leads to an increase in permeation. For fuel cells this effect has been frequently investigated as a function of the relative humidity of the feed gases e.g. Refs. [4,6,8,9].

Most of the reported permeation measurements were conducted with pure permeation cells, without external applied current. Therefore, the effect of current density on gas permeation has been rarely investigated. Some research groups measured the hydrogen in oxygen volume fraction within the anode over wide current density ranges e.g. Refs. [1,2,13,14]. The present work shows that this hydrogen volume fraction can be used as an easy, in-situ crossover measurement.

However, the strong effect of current density on gas permeation during water electrolysis, which was observed by Sakai et al. [4], was not further characterized in detail. Sakai et al. [4] suggested that an increase of the current density leads to an increase in local pressure within the catalyst layer due to the gas evolution and that this local overpressure results in an increase in gas permeation. The same explanation was proposed by Schalenbach et al. [1]. Schalenbach et al. [1] introduced in their electrolysis model an empirical pressure enhancement factor, which was parameterized with experimental data. Both research groups stated that the local pressure increases with current density about several bar per A/cm^2.

The present contribution presents hydrogen volume fraction measurements of the anode product gas during PEM water electrolysis. Measurement series were conducted with current densities from 0.05 to 1 A/cm^2 at different temperatures between 30 and 80 °C and cathode pressures in the range of 1–31 bar. In the following experimental section the setup and method for the permeation measurement are described. Then the experimental results are discussed and compared to available literature data. Special focus is on the influence of current density on hydrogen permeation in dependence of temperature and cathode pressure. After that, potential reasons for the observed effects are reviewed and discussed, such as the previously mentioned local pressure enhancement theory. Finally, a promising explanation for the strong permeation increase is suggested that is based on supersaturation effects in the catalyst layer, which originates from mass transfer limitations.

Experimental

Setup

A single, circular designed PEM water electrolysis cell (Sylatech Analysetechnik GmbH, type ZE 200) was used for the permeation experiments. Instead of flow fields, expanded titanium meshes are implemented on both sides with a thickness of 1 mm. Furthermore, the cell contains on the anode a porous titanium transport layer (PTL) and on the cathode side a graphite PTL with thicknesses of 1 mm and 380 μm, respectively. Within the cell a catalyst coated membrane (CCM) type fumea EF-40 (FuMa-Tech GmbH) with an active area A of 63.6 cm^2 was used. Before usage the CCM was activated as it was recommended by the manufacturer. The membrane of the applied CCM is a reinforced perfluorosulfonic acid (PFSA) membrane with a thickness of δ^m of 230–250 μm, a water uptake of round about 30 wt.% and an equivalent weight of 910 g/mol. The catalyst material on the anode and cathode are Ir- and Pt-based, respectively.

In Fig. 1 the experimental setup is schematically shown. The anode gas/water mixture was cooled down to 25 °C. Subsequently, the liquid water was separated from the product gas. Hydrogen volume fraction of the dried anodic product gas was analyzed with a K1550 gas sensor (Hitech Instruments) based on a heat conductivity measurement. This sensor has a measurement range of 0–5 vol.% H$_2$ in O$_2$, due to safety reasons, since the lower explosion limit (LEL) lies at about 4 vol.% H$_2$ in O$_2$ [17]. The sensor has a measurement error of $\Delta\phi_{H_2} = \pm 0.1$ vol.%.

A test station (Greenlight, E100) supplied the cell with tempered water circulation feeds of 130 g/min on both anode and cathode side. Because of the porous cell structure the anode inlet pressure was measured between 1 and 3 bar depending on temperature and current density. The temperature of the feed water was set to 30, 45, 60 and 80 °C and the
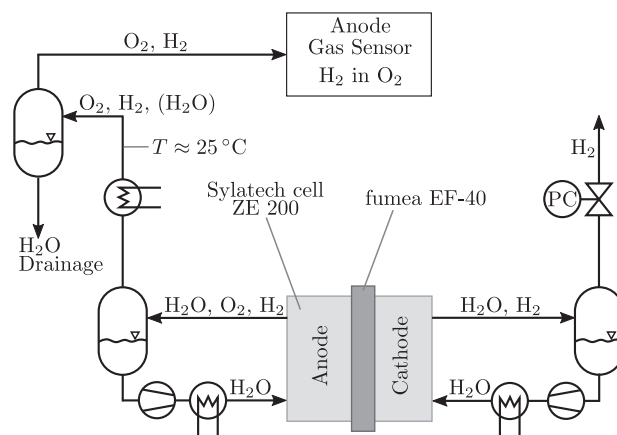

Fig. 1 – Sketch of the experimental setup with the most important appliances.