# Sensor for dissolved hydrogen
# with in-line calibration in aqueous media

by

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## 1 Introduction

Hydrogen is becoming increasingly important as a process component in various areas of technology, often in relatively new applications. One example is in thermal power plants where the residual hydrogen concentration in boiler feedwater or water-steam-loop of power plants acts as an indicator of corrosion [1,2,3] or controlling the hydrogen concentration in the primary loop of a nuclear power plant [4,5]. Others include the removal of nitrate ($NO^-_3$) from drinking water [7] or catalytical removal of oxygen from water [6] where hydrogen concentration is used to monitor the progress of the catalytical reduction process. In the future, hydrogen measurement is also likely to become important in other wastewater treatment processes involving reduction [8]. Continuous quantitative measurement of dissolved hydrogen requires a specifically designed instrument. In particular, the design of such an instrument places important demands on its reliability, ease of calibration and use, measuring range, maintenance and mechanical strength.

Calibration is especially important in the overall performance of the system. Ideally, the instrument should have in-line calibration, without the need for external calibration devices or changes in the plant's operating conditions. Simple, rapid calibration with automatic sensitivity correction allows the instrument to be calibrated more often, with consequent gains in performance and reliability.

The hydrogen in a water/steam loop of a power plant is mainly produced by the reaction between iron and water or steam. One of several possible reaction steps for the proceedings according to the plant operation state is:

$$3\ Fe + 4\ H_2O \Leftrightarrow Fe_3O_4 + 4\ H_2 \qquad (1)$$

This reaction (1) is named Schikorr-reaction. Simultaneously with hydrogen a more or less compact ($Fe_3O_4$) layer is building. This magnetite layer is chemically very resistant and protects the iron underneath from further attacks because it is of insoluble in water and because of its dense surface. Thus, in this case, we have a desirable (corrosion)reaction. Consequently, it is the aim to operate the water system of a power plant under such parameters that the magnetite protective layer is developed fast and compact. Therefore, under normal conditions there should be seen only least hydrogen. These amounts of residual hydrogen arise because under the influence of the temperature iron atoms diffuse through the magnetite layer that is only a few micro-meter thick (approximate 50 µm). To build this protective layer several chemical conditionings of the water/steam loops are required. For example, it is necessary to reduce the conductivity to less than 0,25 µS/cm, that means to use full deionised feed water. In addition to the alkaline medium (most ammonia $NH_3$) to set the pH value approximately from 8 to 9, oxygen has to be dose simultaneously into the boiler feedwater. This oxygen, which is either free or bounded (e.g. hydrogen peroxid $H_2O_2$), is necessary for the stability of the ($Fe_3O_4$) protective layer and should be around 50 µg/l to 150 µg/l. This operation of a boiling system is named combi-operation.

Under normal operation conditions the hydrogen concentration ranges between a few µg/l, partly less than 1µg/l and several hundred µg/l during start-up operation because the protective layer is not complete until approximately 50 hours of operation. For an optimal development of the magnetite layer and therefore for a later trouble-free operation it is important to follow the build-up phase of the protective layer. For a correct hydrogen measurement it is important that the instrument has no influence if oxygen is presence.

But, if the measured hydrogen values are greater 10 µg/l to 50 µg/l under normal working conditions, continued corrosion reactions will take place in the system which destroy the tube or boiler material. As well as load changes can damage the magnetite layer on the basis of pressure spiking or stream variance under hydrogen creation. In figure 1 the hydrogen contents over a 3-day term is shown under normal operation conditions at a Berlin power station. Whereas in figure 2 the measured high hydrogen concentration point at processes of corrosion in the system. These measurements

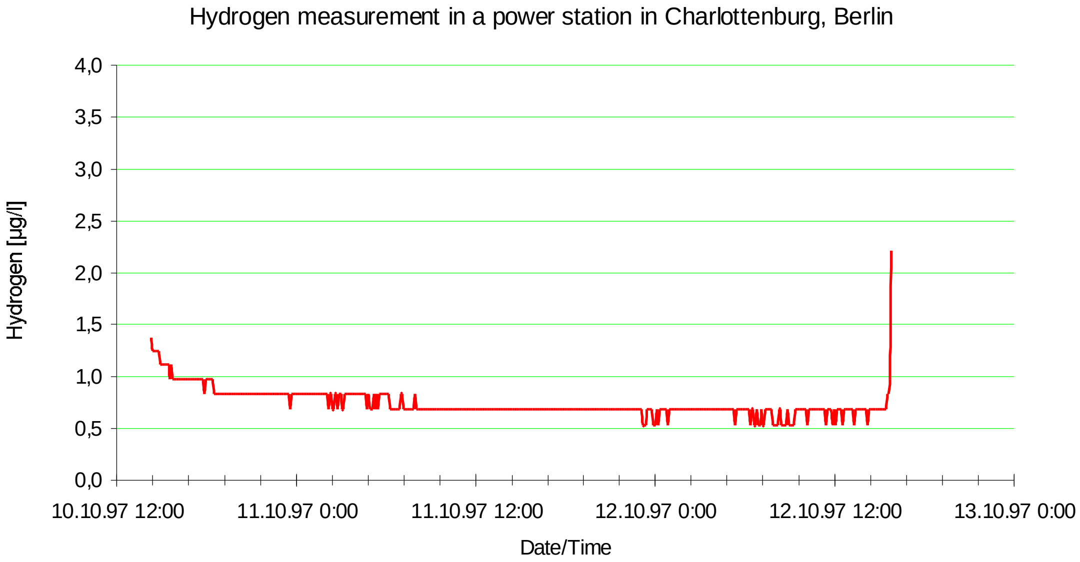

Figure 1

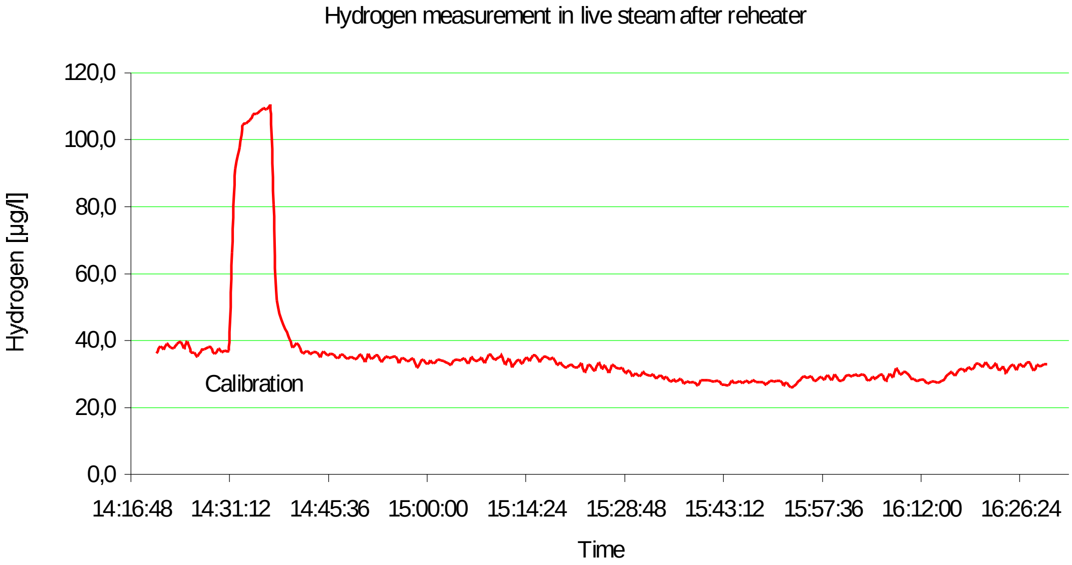

Figure 2

were carried out in live steam after reheater of a heat power plant. At this measurement the in-line calibration is clearly indicated. From the rise of the measure signal during the calibration process the present sensor sensitivity is determined and adjusted if necessary.

Thus, the dissolved hydrogen concentration gives quantitative and qualitative evidence of the rate of corrosion and therefore corresponds to the buildup or destruction of the protective oxide layer inside pipes and boiler tubes through chemical attack or thermal influence respectively.

A further important parameter of operation for the water quality presents the iron contends in the water circuit, especially with regard to load changing. The determination of the iron is a large-scale and lengthy process, which particular general conditions prescribes for the implementation, e. g. load changes or changes of the flow rate of the samples. The analyses are frequently not carry out continuously (on-line), e. g. by means of ICP after sample preparing, so that a temporal assignment to the iron values by virtue of status of operations is often only difficulty possible. According to equation (1) a exact relation exists between hydrogen concentration and exchange of iron, a hydrogen measuring should allow information's about iron values, which take place continuously of course. As part of a diploma work [9] investigations were performed to show, whether a relationship exist between measured hydrogen concentrations and chemically certain iron values. Figure 3 shows the determined values; it is to be noticed here, that the absolute values at these measuring points are very low, which the chemical determination of the iron values makes more complicate. Tendency-wise the change in the iron contends are reflected also in the corresponding hydrogen values, how expects.

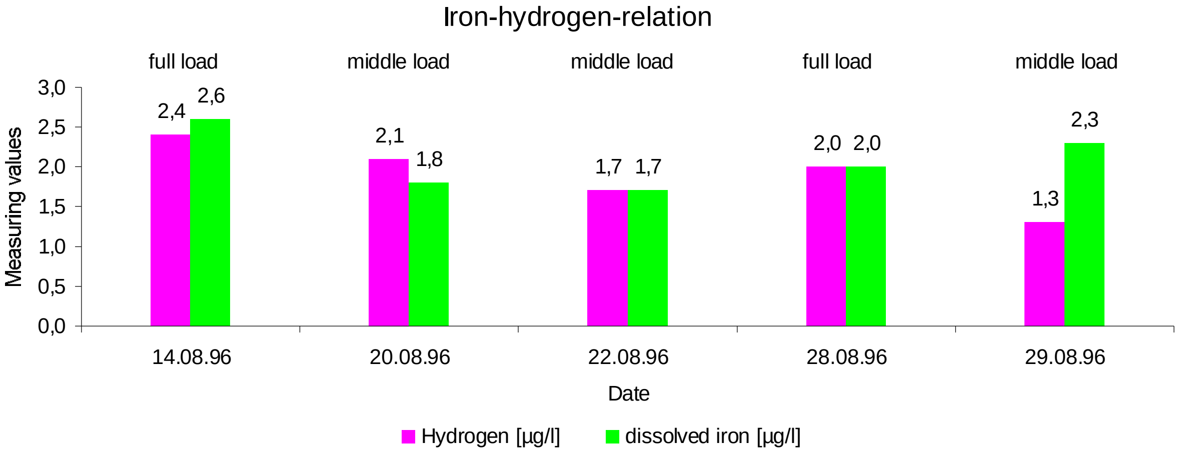

Figure 3

The hydrogen measurement in the primary circuit of a nuclear power plant works under other point of views. Molecular hydrogen ($H_2$) ranging from 2 mg/l to 4 mg/l is added to the reactor water. It has the task to eliminate the oxygen which is created by radiolysis. The hydrogen also reduces the electro-chemical potential (ECP) between the tube material and the bulk of the reactor water and decreases the corrosion proneness of the material. Material tests in relation with hydrogen dosage have clearly shown that intergranular cracking of sensitizing steel is avoided. Figure 4 shows the hydrogen concentration in the reactor water and in the reactor pressure tank of the nuclear power plant in Gronde, Germany.

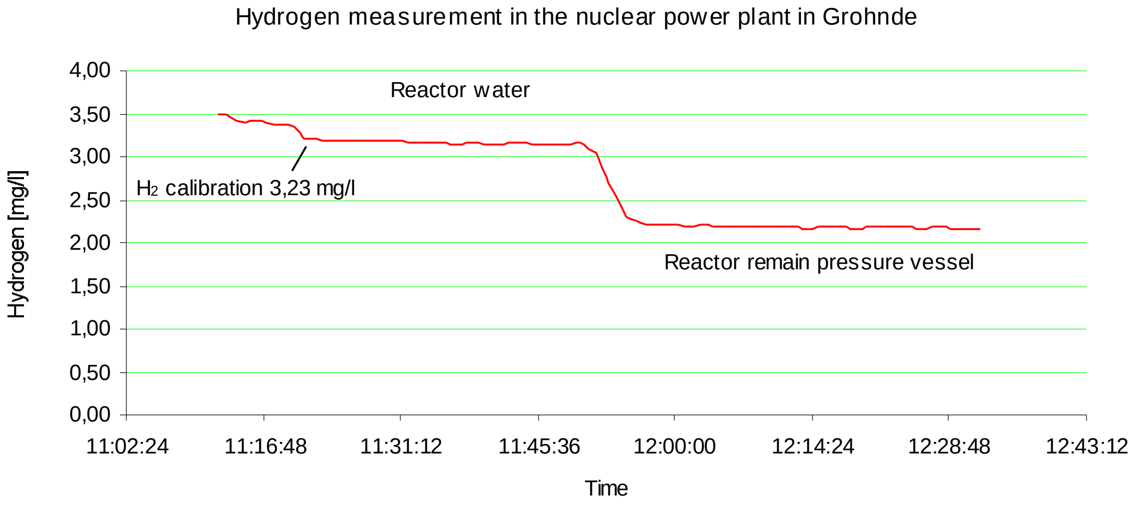

Figure 4

But also hydrogen concentrations of around 20 mg/l occur, for example during the denitrification (removal of nitrate $NO^-_3$) of drinking water or during the catalytic reduction of oxygen from product water, e.g. oxygen fee water for the beverage industry or for the boiler feedwater treatment in power plants. Therefore, dissolved (molecular) hydrogen is added to the oxygen content water. With the help of direct interaction with a catalyst the molecular bonding forces of the hydrogen molecule break up and the now present elementary hydrogen reacts with the oxygen to water (oxyhydrogen gas reaction).

The aim of the denitrification is to reduce nitrate or nitrite ($NO^-_2$) to nitrogen by hydratation catalysts and hydrogen without building harmful products (2).

$$2\ NO_3^- + 5\ H_2 \Rightarrow N_2 + 2\ (OH)^- + 4\ H_2O \qquad (2)$$

These reactions take place on the surface of noble metal catalysts (e. g. palladium or platinum at $\gamma$-aluminum oxide basis or active coal). Figure 5 is showing this proceeding schematically. Especially, for the correct performance and for economical aspects of the reduction processes, the correct amount of stoichiometric hydrogen is important. Additional, the hydrogen measurement at the outlet can control the efficiency of the catalysts in the reactor.

Schematic for nitrat removal

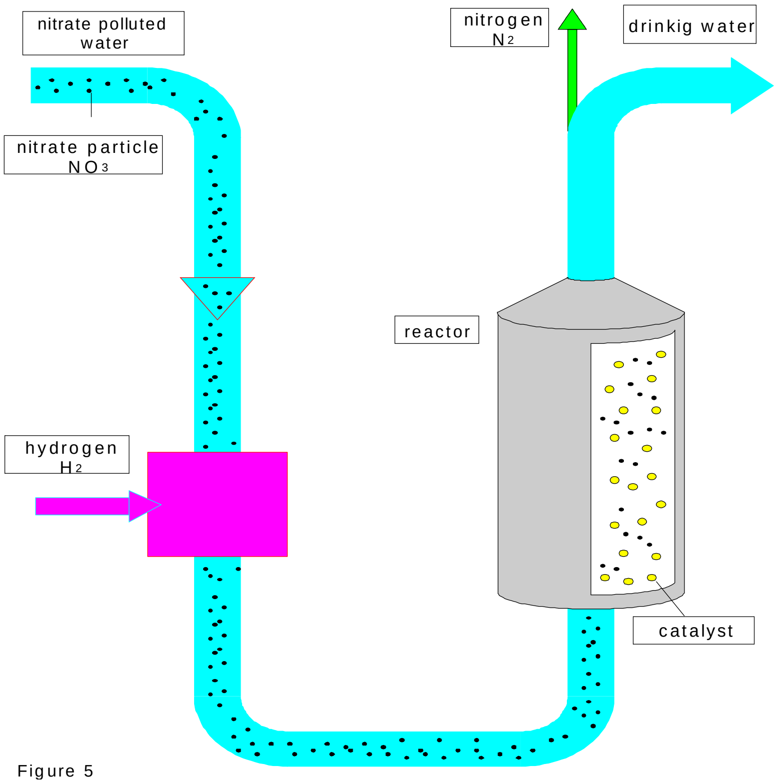

Figure 5

## 2 Basic information

This new, patented instrument HYDROLYT LP 100 [10] functions in a potentiostatic mode with an open three-electrode system. The measuring electrode is made from solid titanium coated with platinum, the counter electrode is made of stainless steel and the reference electrode is silver/silverchlorid [11]. The use of an open measuring electrode means that there are no membranes to block.

For the measurement of dissolved molecular hydrogen ($H_2$) the fluid medium flows into the coaxial measurement cell between the platinum measuring electrode and counter electrode (figure 5). If the measuring electrode is at the correct potential, hydrogen is oxidized in the interphase boundary layer. The electrochemical reaction may be represented qualitatively as (3):

$$H_2 + 2 \cdot H_2O \Leftrightarrow 2 \cdot H_3O^+ + 2 \cdot e^- \qquad (3)$$

Equation (2) describes the anodic oxidation of hydrogen in acid media. The characteristic potential for this reaction - the potential at which hydrogen oxidation occurs in preference to other competing reactions - is measured by holding the potential of the measuring electrode steady with a potentiostat and comparing its value with that of the reference electrode. Under these conditions the rate of the electrochemical reaction is limited mainly by the rate of diffusion of hydrogen molecules to the electrode and the rate the of diffusion of the reaction products $H_3O^+$ away from the electrode surface, so that the mass transport proceedings are dominated [10].

When the potential of the measuring electrode lies within the ‘diffusion-limiting-current’ area (figure 6), the electrochemical cell delivers an electric current whose size depends linearly on the concentration of dissolved hydrogen. The hydrogen molecule, which is transformed in $H_3O^+$, discharges at the counter electrode surface in the reverse electro-chemical reaction (1). This current, which is measured by the instrument's electronic processing unit, is known as the diffusion-limiting current, $I_{diff}$:

$$I_{diff} = f(c_{H_2}) \qquad (4)$$

This diffusion-limiting current mainly depends on the mass transport of the electrochemically active components, and hence on the hydrodynamics in the measuring cell. Therefore it changes significantly with the temperature and flowrate through the measuring cell. These relations can be described quantitatively at a defined cell geometry and state of flow conditions partially with methods of similarity theory [11].

A second important influence on the measurement is the condition of the electrodes, in particular the adsorptive and oxidative state of the electrode surface layer. This is independent of the flow conditions; instead it depends on the voltage between electrode and electrolyte and on the material of which the electrode is made, furthermore on sample matrix particularly either pH-value and the preliminary condition of the platinum sensor. These relations are manifold and are time dependent, so that they withdraw a general quantitative description with justifiable expense. On the other hand, a platinum metal as electrode material is without practical alternative, here a must. In practice the flowrate $f(D)$ and temperature $f(T)$ vary over wide ranges, but the instrument detects these parameters with built-in sensors.

But also the sample matrix can both be fundamentally different as well as currently. Those previous mentioned problems can be described by finding an empirical relation $I_{diff} = f(D)$ and $I_{diff} = f(T)$ from the experimental data. For applications this approximation will be described by a general mathematical function. With the help of calculation programs in the instrument's electronic processing unit the present electrical measured current become convert in the correct concentration value, for which also the notion compensation is common. For the communication with external equipment's analog and digital interfaces available which guarantee a high automatize degree of the sensor system.

## 3 The measuring system

Upstream of the measuring cell is the calibration cell (figure 6) [13, 14]. This consists of two stainless steel electrodes, between which water (sample) is dissociated by a constant controlled current. According to Faraday's law, the rate of hydrogen production in the calibration cell is directly proportional to the current. The electric current is exactly defined in the way, that a known amount of difference of the hydrogen concentration $\Delta c_{H_2}$ in the present sample flowrate is added to the present current level. This calibration current can be chosen depending on the applicable measuring range. A constant electric current of 26,8 mA, for example, produces an increase in the hydrogen concentration of 100 µg/l at a flowrate of 10 l/h. This gives rise to a corresponding increase in the output current from the measuring cell, allowing the processing unit to calibrate the system automatically.

At the outlet of the calibration cell is a narrow diffusor tube which is mixing the fluid to ensure a uniform hydrogen concentration. After passing through the flowmeter the fluid flows into the measuring cell, passing through the annulus between the platinum measuring electrode and counter electrode. The dimension of the annulus has been optimized to give repeatable, laminar flow between the electrodes.

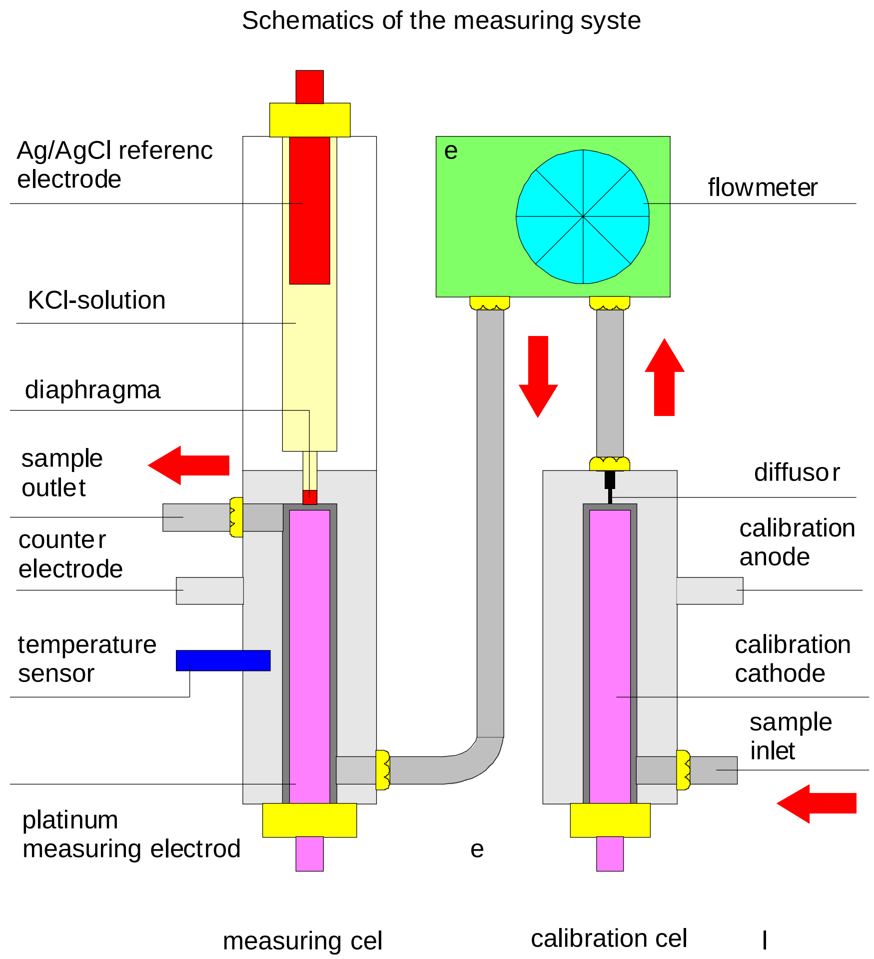

Figure 6

In co-operation with the Technische Fachhochschule Berlin (TFH) typical potential-current diagrams of the anodic hydrogen reaction at galvanic coated measuring electrodes were carried out (figure 7) to define the optimal working area of the electrode system.

For practical analyses the entire range of voltage in the diffusion-limiting current area is not generally available. In the first place the plateau area is limited by the anodic oxygen and cathodic hydrogen envelopment. Instead, a specific voltage value is chosen based on the electrode design and, preferably, the pH range in which the instrument will operate. Furthermore, it must carry out an optimization of the „zero-indication" ,here named residue current Io, if no hydrogen is present in the sample. Especially it must lead to an optimization of the catalytic behavior of the platinum electrode surface and reproducibility during drastic change of hydrogen concentration, for example, in case of low hydrogen concentration during starting and finishing the calibration procedure. In this case the platinum electrode shows more or less a hysteresis which can be reduced by optimization of the measuring potential. This optimization is also influenced through the geometric design of the measuring cell. In figure 8 a typical curve of a diffusion-limiting current as a function of hydrogen concentration is shown. It is approximately a straight line, which is theoretical expect, showing how effectively the instrument can be when operating at an optimized voltage for the measuring electrode.

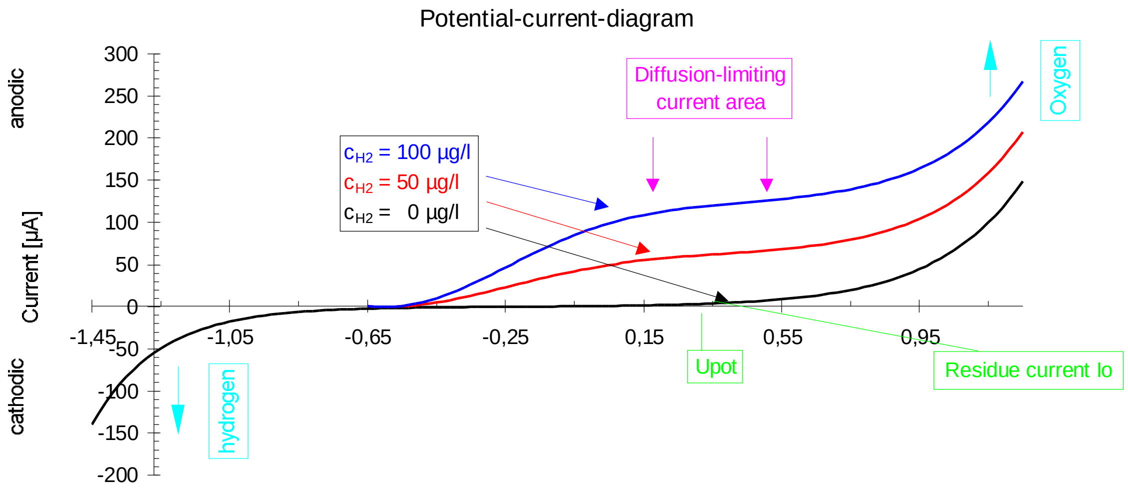

Figure 7

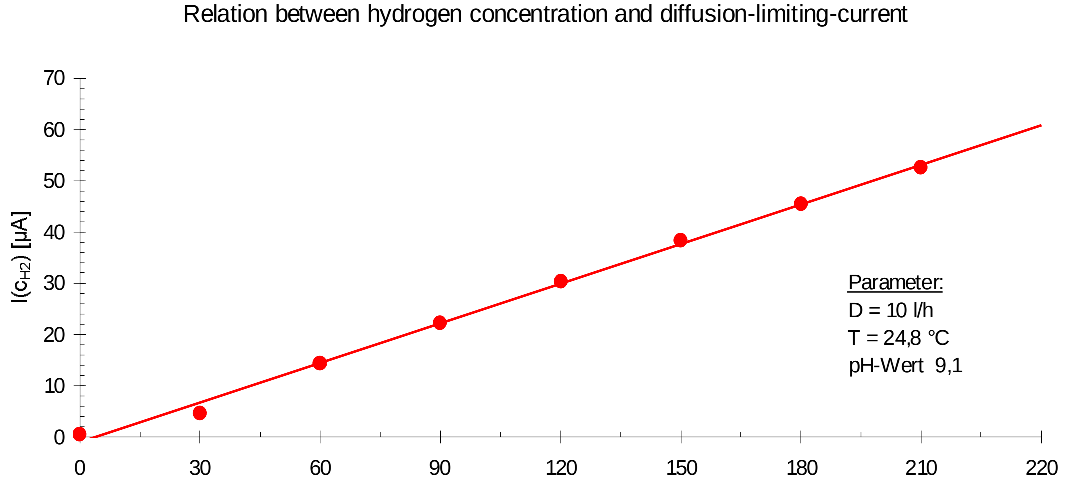

Figure 8

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